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PHYSICAL REVIEW.

ON THE MAINTENANCE OF COMBINATIONAL VIBRATIONS BY TWO SIMPLE HARMONIC FORCES.

By C. V. Raman.

Introductory.

In a previous publication in this Review[1] I dealt with my experimental investigations on a new class of forced oscillations maintained by periodic variation of spring, of which the well-known phenomenon of the maintenance of vibrations by forces of double frequency (dealt with by Faraday, Melde and Lord Rayleigh) is a specific case. Working with the same apparatus as is used for one of the forms of Melde's experiment, I showed that a simple harmonic force acting longitudinally upon a stretched string could maintain its vibrations when the frequency of the free oscillations of the string in any given mode, is sufficiently nearly equal to any integral multiple of half the frequency of the fork. To illustrate and explain the manner in which such maintenance is effected, a series of photographs were published with the paper, showing simultaneous vibration-curves of the exciting tuning-fork and the maintained motion of the string, in which the natural frequencies of the latter were various integral multiples of half the frequency of the former. From these photographs and the mathematical discussion, it became clear that a very important part in the maintenance of the motion is played by certain subsidiary components introduced into it under the action of the variable spring. The principal component of the maintained vibration together with the subsidiary motions thus introduced could, it was shown, be arranged in the form of a Fourier series, the difference of frequency between the successive terms being that of the variable spring itself.

The successful investigation of this class of resonance-vibrations suggested further experiments with systems subjected simultaneously

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[1] "Some Remarkable Cases of Resonance," Physical Review, Dec., 1912.

to *two* simple harmonic forces of differing frequencies varying the spring. These have been productive of some very interesting results and will form the subject of the present paper.

EXPERIMENTAL ARRANGEMENTS.

As mentioned above, the idea underlying the investigation now to be described was to subject a system, having a frequency of vibration that could be adjusted to any desired value over a wide range, *e. g.*, a stretched string, simultaneously to two simple harmonic forces of known frequencies varying its spring, and then to observe and record the various cases in which the state of equilibrium which usually obtains becomes unstable and the system settles down into vigorous vibration.

The experimental method adopted was extremely simple. Two electrically-maintained turning-forks were used. These stood on the table at some distance apart with their prongs vertical, in one plane, and directions of vibration parallel. A fine silk or cotton string, one or two metres in length, was stretched horizontally between the two forks, its extremities being attached to one prong of each fork (*i. e.*, to those nearest to each other). The tension of the string when the forks were at rest could be readily adjusted by merely sliding one fork slightly towards or away from the other along the table. Since the prongs of the fork are vertical and the string is parallel to their direction of vibration, we have as the result when the forks are excited, that the tension of the string is periodically varied by the vibrations of both simultaneously.

Of course, with the arrangements described neither of the forks, whether acting by itself or conjointly with the other, tends *directly* to displace the string from its position of equilibrium. They vary the tension of the string, but the latter remains undisturbed so far as transverse movement is concerned, except when the initial tension, *i. e.*, the frequency of free oscillation of the string, is adjusted so as to coincide more or less accurately with certain values which we may for convenience term "resonance frequencies," leaving the justification of this phraseology to be dealt with later.

Certain of the resonance-frequencies should obviously be multiples of half the frequency of one or the other of the forks by itself. For, each of the forks acting alone can maintain a vigorous vibration in a number of cases as shown in the paper referred to above, and this vibration is excited and maintained under suitable conditions even in the presence of the other periodic force varying the spring. To put it mathematically, if the frequency of free oscillation of the string in any given mode is sufficiently nearly equal to either $\frac{1}{2}rN_1$ or $\frac{1}{2}sN_2$, where N_1, N_2 are the frequencies of the forks, r, s, being any positive integers, we would get resonance-vibrations as already shown. That certain of the resonances observed are of this class, can readily be verified by stopping the fork which does not play a part in the maintenance, when the vibration of the other fork continues to sustain the motion of the string.

Besides the resonances of the kind described in the preceding paragraph, the observer is surprised and delighted to find, even at a first trial of the experiment, a large number of other cases of vigorous maintenance which have evidently to be ascribed to the joint action of the two forks on the string. Their variety and number is extraordinary, and these, together with the way in which they come rapidly following one another particularly at the higher frequencies, remind the observer, by a vivid analogy, of the lines in a complicated spectrum-series. It is readily guessed at once that these are cases of "combinational" resonance in which the frequency of the principal term in the maintained motion is related *jointly* to the frequencies of both the forks. This fact is readily verified by experimental investigation as described below, and the results obtained can be stated with generality thus. Under suitable conditions the equilibrium of the system becomes unstable and a vigorous motion is maintained if the frequency of free vibration in any given mode is sufficiently nearly equal to $\frac{1}{2}rN_1 \pm \frac{1}{2}sN_2$, where r and s are *positive* integers. The degree of accuracy of adjustment necessary for maintenance increases as r and s increase. Where the positive sign applies we have "summational" resonances. With the negative sign we have "differential" resonances. The frequency of the maintained motion is *exactly* equal to $\frac{1}{2}rN_1 \pm \frac{1}{2}sN_2$, where r and s have the values assigned.

Of course N_1 and N_2, which are the frequencies of the forks, do not in general stand in any simple arithmetical ratio, and the cases of "combinational" resonance described in this paper could in almost all cases be recognized and distinguished from "simple" resonance due to either of the forks acting alone by a peculiar appearance of "flicker" due to the presence of *small* components of very low frequencies in the motion. Even if this method failed, there is the alternative test of stopping either of the two forks when a "combinational" is instantly extinguished, whereas a "simple" resonance is only abolished by stopping *one* of the two forks, and not *either*. One very characteristic feature which was noticed in the experiments was that while resonance-vibrations of the *summational* class were obtained with great ease up to fairly high orders and vigorously maintained, *differential* vibrations were not nearly so readily maintained, and it was found necessary, in order to realize them to arrange matters so that none of the other resonances due to the forks, simple or summational, lay in the neighborhood of the one sought for and could therefore extinguish it, the former being maintained by preference. The result noticed above is an inversion of the ordinary experience in acoustical work with combinational tones in which it is found that differentials are generally stronger and easier to demonstrate than summationals. The theoretical explanation of the effect will be discussed later in this paper.

PHOTOGRAPHIC RECORD OF COMBINATIONAL VIBRATIONS.

In order to demonstrate that the frequency of maintenance is that given by the combinational formula referred to above, the method of vibration-curves was used. Arrangements were made to obtain simultaneous photographic records of the vibration of the two forks and of the maintained oscillation of the string. These records incidentally throw light on the *modus operandi* of the maintenance. The disposition of the apparatus employed is shown in Fig. 1.

T_1 and T_2 are the two forks which stand with prongs vertical on the table. The string is stretched horizontally between the inner prongs of the forks as shown.

To enable its plane of vibration to be brought into the vertical at pleasure, the following very simple device is adopted. Each end of the string is attached to a loop of thread which is passed over the prong of the fork, instead of directly to the prong itself. The result of this mode of attachment is that the frequencies of vibration in the horizontal and vertical planes differ slightly, and this has the desired effect of keeping the vibration confined to the vertical if the tension of the string is suitably adjusted in each case. Immediately in front of the string is placed a camera, the plate-carrier of which has been removed, and which carries instead a square sheet fitted with a narrow vertical slit S as nearly as possible contiguous to the string. The light from an electric arc emerges from the nozzle of the lantern L; and is then divided into three parts.

1. One part passes first through the vertical slit S, then through the lens of the camera carrying it, and after suffering reflexion at the fixed mirror M passes on to the lens of the moving-plate camera DD (to be described below).

2. The second part is deflected by the mirror M_1, and after passing through a narrow horizontal slit S_1 suffers reflexion at the surface of a small plane mirror M_2 attached to the prong of the fork T_1 and is finally deflected by the mirror M_3 to the lens of the camera DD.

3. The third part after deflexion by the mirror M_4 passes through the

horizontal slit S_2, and thence after reflexion at a plane mirror M_5 attached to the prong of the fork T_2 passes on to the camera *DD*.

By suitably adjusting the position of the slits S_1 and S_2 and the distance between the slit *S* and the lens of the camera carrying it, it was found possible without the use of any additional collimating lenses to obtain in the focal plane of the camera *DD* real images of the vertical slit *S* and of the horizontal slits S_2 and S_1, the images of the latter being formed respectively above and below the images of the vertical slit *S*. A narrow vertical slit placed in the focal plane of the camera immediately in front of the ground-glass or its substitute, the photographic plate, cuts off everything except two brilliant spots of light, one for each fork, and between them the image of the illuminated vertical slit crossing which is seen the shadow of the string when at rest. The plate-holder can be moved (by hand) in horizontal grooves behind the slit in the focal plane, and when the forks are set in vibration we can thus obtain

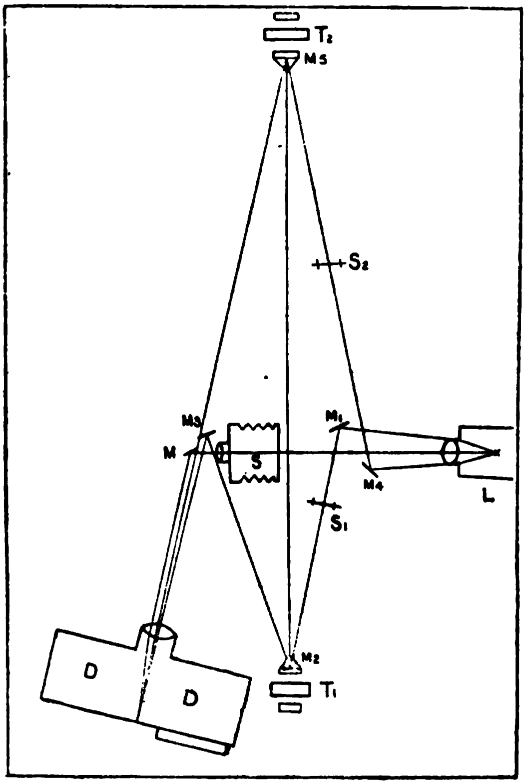

Fig. 1.

Apparatus for the production and photographic record of combinational vibrations.

photographic records of simultaneous vibration-curves of the string and forks.

By counting the number of swings shown in each of the three curves appearing in a record, the relation between the frequencies of the forks and that of the maintained motion of the string can be observed and tested with the exact combinational formula $\frac{1}{2}(rN_1 \pm sN_2)$. Illustrations of this method will be given later.

ISOLATION OF INDIVIDUAL TYPES.

As already mentioned above, the vibrations of the summational class are obtained with great ease. Taking only the first four types of summationals, *i. e.*, with $r = 1$ or 2 or 3 or 4 and $s = 1$ or 2 or 3 or 4, we have 4×4, *i. e.*, 16 distinct types possible, or if we include the cases in which either r or s is zero, *i. e.*, those of resonance due to each of the forks acting by itself, 24 distinct types. In practice summationals of types even higher than the fourth are distinguishable. For each of these various frequencies of vibration, the string may divide up into one, two, three or more ventral segments, according to circumstances. We have therefore a very large number of cases in which resonance is possible, and it is a matter for considerable surprise that it should be at all possible (not to speak of its being quite easy) to isolate in experiment any one of these manifold modes and frequencies of vibration and obtain distinctive photographic records of the same. The explanation of this result is very instructive. It rests upon the following facts: for each of these summationals there is a limited and fairly well-defined range of frequency within which the natural frequency of the system should lie if maintenance is to be possible. If the natural frequency of the system lies within this range, the vibration is vigorously maintained. If outside it, the summational does not put in an appearance. The range becomes narrower and narrower as we go higher up the scale and is smallest in the very region where the summationals are relatively speaking most numerous. This effectually prevents their crowding in unduly upon each other.

The facts mentioned in the foregoing paragraph sufficiently explain the successful isolation of the several vibrational types. After a little practice it will be found easy to arrange that any given member of the series of summationals (if not of too high an order) is obtained and vigorously maintained. The necessary guide to the proper adjustment of tension is to be had by noticing the tensions at which the "simple" resonances in various modes due to either of the forks acting alone occur, and by drawing up a table of frequencies of the summational vibrations it is a simple matter to get the right tension for any one of them.

In practical work, it will be found a useful device (besides adjusting the tension of the string to correspond with the frequency required), to regulate the amplitude of vibration of the forks in a suitable manner. This is readily done, if the forks are electrically maintained by altering the driving current or the position of the contact-maker. The formula to be borne in mind is, if r is large and s is small, to work the N_1 fork vigorously and the N_2 fork with quite a small amplitude of vibration: vice-versa if r is small and s is large. If r and s are to be nearly equal, the amplitudes are to be roughly commensurate with the values of r and s. This regulation of the amplitude ensures the desired summational being obtained without fail, and unaccompanied by other modes of vibration.

Vibration-Curves of Summationals.

Figs. 3 to 13 exhibit the photographic records for all the nine summationals comprised within the first three types, for one summational of the fourth type and one of the fifth, *i. e.*, eleven photographs in all. The two forks used had frequencies of 60 and 23.7 respectively per second. In the reproductions their vibration-curves appear white on a dark ground and that of the string dark on a bright background. The two former appear one on each side of the latter. It is obvious from an inspection of the vibration-curves of the string that in each case the principal part of the maintained motion is accompanied by subsidiary components. These components are introduced by the alteration of the character of the maintained motion due to the imposed variable spring, and it will be seen from the theoretical discussion to follow that they act as vehicles for the supply of energy to the system. In a few cases their periodicity is fairly evident to inspection.

Fig. 3.—This is the first and most important summational, the frequency of maintenance being equal to the sum of half the frequencies of the forks. This is readily shown by counting the swings shown on each curve. Thus—

Summational $\frac{1}{2}N_1 + \frac{1}{2}N_2$.

	Fork N_1.	Fork N_2.	String.
Number of swings	17.50	6.90	12.23
Calculated frequency	60.0	23.70	41.95
Observed frequency	60.0	23.70	41.93

An inspection of the vibration-curve of the string clearly shows the periodic flattening and sharpening of the maintained motion under the joint action of the components of the variable spring.

Fig. 4.—This shows the next higher frequency of maintenance, summational $\frac{1}{2}N_1 + N_2$, frequency 53.7 approximately.

Fig. 5 shows the summational $\frac{1}{2}N_1 + \frac{3}{2}N_2$, frequency 65.6.
Fig. 6 shows the summational $N_1 + \frac{1}{2}N_2$, frequency 71.9.
Fig. 7 shows the summational $N_1 + N_2$, frequency 83.7.
Fig. 8 shows the summational $N_1 + \frac{3}{2}N_2$, frequency 95.6.
Fig. 9 shows the summational $\frac{3}{2}N_1+\frac{1}{2}N_2$, frequency 101.9.
Fig. 10 shows the summational $\frac{3}{2}N_1 + N_2$ frequency 113.7.
Fig. 11 shows the summational $\frac{3}{2}N_1 + \frac{3}{2}N_2$, frequency 125.6.

Fig. 12 shows one of the summationals of the fourth type, frequency $2N_1 + \frac{1}{2}N_2$, *i. e.*, 131.9.

Fig. 13 shows one of the summationals of the fifth type, frequency $2N_1 + \frac{5}{2}N_2$, *i. e.*, 179.3.

VIBRATION-CURVES OF DIFFERENTIALS.

Using the two forks of frequencies 60 and 23.7 it was not found possible to obtain any cases of differential resonances, as these lay in the region in which the primaries and summationals were present and were strongly maintained in preference. After some trial, however, using forks of adjustable frequencies with which the frequencies of possible differentials lay far removed from that of the stronger resonances due to either of the forks alone or their summationals, I succeeded in isolating two cases of differential resonance. Fig. 14 represents the differential of the first type, frequency $\frac{1}{2}N_1$ and $\frac{1}{2}N_2$, being respectively 128 and 23.7. Fig. 15 represents a differential of the second type, frequency $N_1 - N_2$ being 92.3, the frequencies of the two forks used, N_1 and N_2, being respectively 128 and 35.7.

It will be seen that in both of these cases, the frequency of the differential is such that it cannot be readily confused with that of any resonances due to either of the forks acting alone or to their summationals.

GENERAL THEORY OF COMBINATIONAL MAINTENANCE.

The equation of motion of a simple oscillatory system having one degree of freedom when subject to two periodic forces varying its spring may be written as

$$\ddot{U} + k\dot{U} + n^2U = 2U[\alpha_1 \sin 2p_1t + \alpha_2 \sin 2p_2t + \beta_1 \cos 2p_1t + \beta_2 \cos 2p_2t] \quad (1)$$

$$= U[2\gamma_1 \sin (2p_1t + E_1) + 2\gamma_2 \sin (2p_2t + E_2)]. \quad (2)$$

It may also be written in the form

$$\ddot{U} + k\dot{U} + (n^2 - 2\gamma_1 \sin \overline{2p_1t + E_1} - 2\gamma_2 \sin \overline{2p_2t + E_2})U = 0. \quad (3)$$

It is instructive to compare the equation of motion as it is written in forms (1) and (2) above, with that of an asymmetrical system subject to double forcing considered by Helmholtz. The latter may be written as

$$\ddot{U} + k\dot{U} + (n^2 - \gamma U)U = 2\gamma_1 \sin(2p_1 t + E_1) + 2\gamma_2 \sin(2p_2 t + E_2) \quad (4)$$

or as

$$\ddot{U} + k\dot{U} + n^2 U = \gamma U^2 + 2\gamma_1 \sin(2p_1 t + E_1) + 2\gamma_2 \sin(2p_2 t + E_2). \quad (5)$$

Equations (2) and (5) are analogous in so far as the term on the right-hand side which represents the "disturbing force" acting on the system is in both cases a function of two variables, *i. e.*, the time, and the configuration of the system: the form of the function is however different in the two cases.

Equations (3) and (4) are analogous in so far as that the coefficient of the third term on the left which represents the "spring" of the system is in both cases a variable. But here the analogy ends, for in one case the variable part of the spring is an independent function of the time, in the other case it is a function of the configuration only.

In any case, however, there is abundant material to suggest that the maintenance of a series of combinational vibrations should be possible under the joint action of two periodic forces of different frequencies varying the spring, and this is fully verified by the results of the experiments described above.

Discussion of Diagram of Periodicities.

The exact process by which the maintenance of the combinational vibrations is effected in these experiments is best understood by analogy with the simpler case of oscillations under variable spring of only one periodicity, and by reference to Fig. 2. In the theory of oscillations maintained by a simple variable spring referred to above, it was shown that when resonance was secured by adjusting the natural frequency of the system to any multiple of half the frequency of the impressed force, the principal part of the maintained motion and the subsidiary components of smaller amplitudes introduced under the action of the variable spring could be arranged in the form of a Fourier series. For example, in the case of the fourth type of maintenance, the equation of motion is

$$\ddot{U} + k\dot{U} + n^2 U = 2\alpha U \sin 2pt,$$

and n being nearly equal to $4p$, we have as the solution

$$\begin{aligned} U = {} & A_2 \sin 2pt + A_4 \sin 4pt + \text{etc.} \\ & + B_0 + B_2 \cos 2pt + B_4 \cos 4pt + \text{etc.} \end{aligned}$$

Similarly in the case of the third type of maintenance where n is nearly equal $3p$ we have

$$\begin{aligned} U = {} & A_1 \sin pt + A_3 \sin 3pt + \text{etc.} \\ & + B_1 \cos pt + B_3 \cos 3pt + \text{etc.} \end{aligned}$$

It will thus be seen that in each case, the subsidiary components introduced under the action of the variable spring proceed by successive differences of $2pt$. The components having smaller frequencies than that of the system were the vehicles for the supply of energy required for the maintenance of the oscillations: those having higher frequencies play no such part, but are equivalent merely to a small alteration in the natural frequency of the system. The components of smaller frequencies are none of them negligible so far as the explanation of the maintenance is concerned: those of higher frequencies can generally (though not always) be safely ignored.

In Fig. 2 each of the points marked corresponds to a frequency of the system at which (to a close approximation) resonance is possible under the sole or joint action of the two components of variable spring in the experiments described above. The diagram also enables us to see at a glance the periodicity of the subsidiary components in the motion in each such case. For, starting at the resonance-point for the case, we move by successive steps of $2p_1$ and $2p_2$ respectively parallel to the two axes, and each point so arrived at represents a component in the motion induced under the action of the variable spring. Only about one fourth of the total number of points in the diagram can be arrived at in this way from a given starting-point. Such of the components as are represented by points lying outside the diagonal square drawn through the

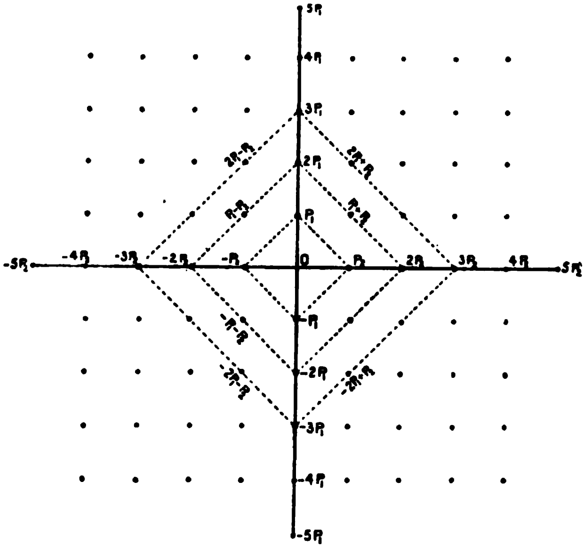

Fig. 2.

Representation of periodicities of combinational maintenance.

resonance-point (as in the specimens shown by dotted lines in the diagram), may be neglected in considering the maintenance of the motion. For example, when considering the case $n = (p_1 + p_2)$ nearly, only the components which are trigonometrical functions of $(p_1 + p_2)t$ and $(p_1 - p_2)t$ need be taken into account to arrive at an approximate solution. It will be seen that alternative paths starting from the same point lead to periodicities having the same value, with or without the sign reversed; and it is this fact and the negligibility of points lying outside the diagonal square in each case that enables a definite solution of the equation of motion to be obtained easily by the method of approximations.

The diagram of periodicities has other uses. It enables us to obtain at a glance an indication of the circumstances under which maintenance can be successfully effected in each case, and to arrange the experimental conditions accordingly. For instance, in the case of motion under one of the components of variable spring alone, we know that the adjustment of the natural frequency of the system with reference to that of the impressed force should be more and more accurate as we proceed outwards along the axes of the diagram and meet the successive resonance-points. In the case of the point p_1 the adjustment should be accurate to the order α, in the case of the point $2p$ to the order α^2, and so on, α being the coefficient of the variable spring (supposed small). The diagram suggests that a similar increase in the accuracy of adjustment would be found necessary as we proceed outwards from the origin in any other direction and meet resonance-points situated on successive diagonals (shown as dotted lines). This indication is amply confirmed both by experiment and by the detailed mathematical treatment. For instance it will be shown below that a degree of adjustment accurate to the order α^2 would be necessary for the point $p_1 + p_2$ which lies midway between $2p_1$ and $2p_2$.

The position of any resonance-point on the diagram is also found to indicate approximately the amplitude of vibration of the two tuning-forks required for successful maintenance.

THEORY OF SUMMATIONALS OF THE FIRST TYPE.

We now proceed to consider the detailed theory of the simplest summational type in which the frequency of maintenance is equal to the sum of half the frequencies of the forks. As already explained, the whole of the string behaves as one unit, in other words, we may write down the equation of motion as that of a system having only one degree of freedom. The equation is

$$\ddot{U} + k\dot{U} + n^2 U = 2U[\alpha_1 \sin 2p_1 t + \alpha_2 \sin 2p_2 t + \beta_1 \cos 2p_1 t + \beta_2 \cos 2p_2 t]. \quad (1)$$

Since by assumption n is nearly equal to $p_1 + p_2$, we may commence building up a solution by putting

$$U = A_1 \sin (p_1 + p_2)t + B_1 \cos (p_1 + p_2)t + \text{etc.} + \text{etc.} \qquad (6)$$

On substituting the first two terms on the right of (6) for U in the right-hand side of equation (1) and expanding the terms in it, we find that none of them is a sine or cosine of $(p_1 + p_2)t$, *i. e.*, represents a force which is competent to excite resonance, if we regard (1) as the ordinary equation of forced oscillations. It is obvious, therefore, that to solve the equation even approximately and explain the maintenance of the motion, we have to take a second subsidiary pair of terms in the expression for U. The frequency of these terms is ascertained at once by reference to the diagram of periodicities given above, and we may then write

$$U = A_1 \sin (p_1 + p_2)t + B_1 \cos (p_1 + p_2)t + A_2 \sin (p_1 - p_2)t + B_2 \cos (p_1 - p_2)t + \text{etc.} \qquad (7)$$

The terms in A_2 and B_2 are of course small compared with those in A_1B_1, yet are sufficiently large to make their presence felt in the vibration-curve pictured previously. They are introduced by the action of *either* of the two periodic components of the variable spring on the fundamental motion, and in their turn maintain the latter by making the requisite supply of energy to the system possible. This can be shown by writing out the equation of the work supplied to the system by the variable spring and that dissipated by frictional forces in an equal time. In the present case it can be shown in a simpler way by merely equating separately the terms of various periodicities on either side of equation (1) after substituting the value of U given by (7).

We have thus:

(writing $n^2 - (p_1 + p_2)^2 = \theta_1$ and $n^2 - (p_1 - p_2)^2 = \vartheta_2$, $k(p_1 + p_2) = \phi_1$ and $k(p_1 - p_2) = \phi_2$ for brevity,

$$\begin{aligned}
\theta_1 A_1 - \phi_1 B_1 &= A_2(\beta_2 - \beta_1) + B_2(\alpha_1 + \alpha_2), \\
\phi_1 A_1 + \theta_1 B_1 &= A_2(\alpha_1 - \alpha_2) + B_2(\beta_1 + \beta_2), \\
\theta_2 A_2 - \phi_2 B_2 &= A_1(\beta_2 - \beta_1) + B_1(\alpha_1 - \alpha_2), \\
\phi_2 A_2 + \theta_2 B_2 &= A_1(\alpha_1 + \alpha_2) + B_1(\beta_1 + \beta_2), \qquad (8)
\end{aligned}$$

It will be seen that these four equations were derived by retaining only terms containing trigonometrical functions of $(p_1 + p_2)t$ and $(p_1 - p_2)t$ and neglecting all others. Before considering the effect, if any, of the neglected terms, it is well to discuss the physical significance of the equations. They give us the three ratios A_1, B_1, A_2, B_2 in terms of the known quantities θ_1, θ_2, ϕ_1, ϕ_2, and α_1, α_2, β_1, β_2, as an approximate solution of the equation of motion and leave us in addition a relation between these "constants" which must be satisfied for steady motion to be possible.

We now proceed to solve the equations. This may, of course, be done in the usual way in terms of certain determinants, but it is more instructive to proceed by an approximate method retaining only terms up to the order of smallness desired. Assuming that α_1, α_2, β_1, β_2 (the coefficients of variable spring) are small, it is obvious from the equations that A_2, B_2 are small compared with A_1, B_1. Further ϕ_2 is a very small quantity compared with θ_2 (which is finite and large), since the former is proportional to k, the coefficient of friction, which must itself be small for maintenance to be possible. We are therefore justified in neglecting ϕ_2 and writing the last two of equations (8) thus:—

$$\begin{aligned} \theta_2 A_2 &= A_1(\beta_2 - \beta_1) + B_1(\alpha_1 - \alpha_2), \\ \theta_2 B_2 &= A_1(\alpha_1 + \alpha_2) + B_1(\beta_1 + \beta_2), \end{aligned} \tag{9}$$

These equations give us the subsidiary components of motion A_2, B_2, in terms of the principal parts A_1, B_1. Substituting these values in the first two of equations (8), we have

$$\begin{aligned} \theta_1 A_1 - \phi_1 B_1 &= \frac{A_1}{\theta_2}\Big[(\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2) + 2(\alpha_1\alpha_2 - \beta_1\beta_2)\Big] \\ &\quad + \frac{B_1}{\theta_2}\Big[2(\alpha_1\beta_2 + \alpha_2\beta_1)\Big] \\ \phi_1 A_1 + \theta_1 B_1 &= \frac{A_1}{\theta_2}\Big[2(\alpha_1\beta_2 + \alpha_2\beta_1)\Big] \\ &\quad + \frac{B_1}{\theta_2}\Big[(\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2) - 2(\alpha_1\alpha_2 - \beta_1\beta_2)\Big]. \end{aligned} \tag{10}$$

Writing

$$\begin{aligned} \theta_1 - \frac{1}{\theta_2}\Big[(\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2)\Big] &= \theta, \\ \frac{2}{\theta_2}(\alpha_1\alpha_2 - \beta_1\beta_2) &= a, \\ \frac{2}{\theta_2}(\alpha_1\beta_2 + \alpha_2\beta_1) &= b \end{aligned}$$

we have

$$\begin{aligned} (\theta - a)A_1 &= (\phi_1 + b)B_1, \\ (\theta + a)B_1 &= -(\phi_1 - b)A_1. \end{aligned} \tag{11}$$

The solution of this is

$$\frac{B_1}{A_1} = \frac{\theta - a}{\phi_1 + b} = \frac{b - \phi_1}{\theta + a} \tag{12}$$

and the eliminant, *i. e.*, the relation between the constants involved which must be satisfied for maintenance to be possible, is

$$\theta^2 - a^2 = b^2 - \phi_1^2. \tag{13}$$

It is interesting to consider a few special cases. For instance put

$$\beta_1 = \beta_2 = 0 \text{ and } \alpha_1 = \alpha_2 = \alpha/2.$$

From (9) we find then that

$$A_2 = 0 \text{ and } B_2 = A_1\alpha/2.$$

Also

$$\theta_1 + \frac{\phi_1^2}{\theta_1} = \alpha^2/\theta_2. \tag{14}$$

From (14) it is evident that θ_1 and ϕ_1 are both of the order α^2/θ_2, *i. e.*, both the friction and adjustment of frequency for resonance must be correct to the second order of small quantities. The equations leave the actual amplitude of the motion indeterminate. In practice both the necessary adjustment of frequency and the determinateness of the amplitude would be secured by the fact that n is not absolutely constant, in other words by the variation of spring existing in free oscillations of sensible amplitude. It will be seen that the term B_2 is small compared with A_1, since the variable part of the spring is small compared with the permanent spring: nevertheless the term B_2 plays a very important part in the maintenance of the motion, being, as is evident from the foregoing equations, the vehicle for the supply of the requisite energy to the system.

It will be seen that the equations cannot be satisfied if $\theta_1 = 0$, as $\theta_1 + (\phi_1^2/\theta_1)$ then becomes infinitely large. According to these equations therefore, resonance is possible only when θ_1 has a small but a definite positive value: *i. e.*, when the frequency of the *free* oscillations is very slightly greater than the sum of the half-frequencies of the two imposed variations of spring. This conclusion would no doubt have to be modified in view of two factors which we have not so far taken into account. First, the neglected terms in the motion which are trigonometrical functions of $(p_1 + 3p_2)t$ and $(3p_1 + p_2)t$, etc., etc. The two terms $(p_1 + 3p_2)t$, $(3p_1 + p_2)t$ which are of the order α when compared with the fundamental motion $(p_1 + p_2)t$ cannot actually assist in maintaining it. This can be shown from very simple considerations. For one thing, they are not introduced by the action of *both* the components of variable spring.

The first is due to one component and the second is due to the other. The components in the restoring force due to their action and which are trigonometrical functions of $(p_1 + p_2)t$ are in such a *phase* that their effect is equivalent to a small increase in the frequency of free oscillations of the system which is some importance when θ_1 is very small.

The second factor which we have to take into account is the variation of spring existing in free oscillations of large amplitude. This, as in the case of oscillations maintained by a single variable spring, when expanded is found to contain both constant and periodic terms. The former are equivalent to a direct increase in the natural frequency of the system, and the latter profoundly modify the effect of the impressed forces and the phases of the respective components in the motion when the amplitude is at all sensible.

THEORY OF SUMMATIONALS OF THE SECOND AND HIGHER TYPES.

As typical of the summationals of the second type we may take the case $n_1 = 2p_1 + p_2$ (nearly). The equation of motion is

$$\ddot{U} + k\dot{U} + n^2U = 2U\left[\begin{array}{l}\alpha_1 \sin 2p_1t + \alpha_2 \sin 2p_2t \\ + \beta_1 \cos 2p_1t + \beta_2 \cos 2p_2t\end{array}\right]. \qquad (1)$$

We may to start with put

$$U = A_1 \sin(2p_1 + p_2)t + B_1 \cos(2p_1 + p_2)t + \text{etc.} + \text{etc.} \qquad (15)$$

As before, we can only solve the equation by taking certain additional terms on the right of (15). A reference to the diagram of periodicities shows that we have to take three additional pairs of terms to get an approximate solution. We may thus write

$$\begin{aligned} U = {} & A_1 \sin(2p_1 + p_2)t + B_1 \cos(2p_1 + p_2)t \\ & + A_2 \sin(2p_1 - p_2)t + B_2 \cos(2p_1 - p_2)t \\ & + A_3 \sin p_2t + B_3 \cos p_2t \\ & + A_4 \sin 3p_2t + B_4 \cos 3p_2t. \end{aligned} \qquad (16)$$

Of course, the terms in A_1 and B_1 are the largest in amplitude. In substituting the right-hand side of (16) for U in equation (1) and writing down in the results, we may use the following abbreviations:

$$\begin{aligned} n^2 - (2p_1 + p_2)^2 &= \theta_1, & k(2p_1 + p_2) &= \phi_1, \\ n^2 - (2p_1 - p_2)^2 &= \theta_2, & k(2p_1 - p_2) &= \phi_2, \\ n^2 - p_2^2 &= \theta_3, & kp_2 &= \phi_3, \\ n^2 - 9p_2^2 &= \theta_4, & 3kp_2 &= \phi_4. \end{aligned} \qquad (17)$$

By equating the various sine and cosine terms on either side of (1) after substitution, we have

$$
\begin{aligned}
\theta_1 A_1 - \phi_1 B_1 &= \beta_1 A_3 + \alpha_1 B_3 + \beta_2 A_2 + \alpha_2 B_2,\\
\phi_1 A_1 + \theta_1 B_1 &= -\alpha_1 A_3 + \beta_1 B_3 - \alpha_2 A_2 + \beta_2 B_2,\\
\theta_2 A_2 - \phi_2 B_2 &= \beta_2 A_1 - \alpha_2 B_1 - \beta_1 B_3 + \alpha_1 B_3,\\
\phi_2 A_2 + \theta_2 B_2 &= \alpha_2 A_1 + \beta_2 B_1 + \alpha_1 A_3 + \beta_1 B_3,\\
\theta_3 A_3 - \phi_3 B_3 &= \beta_1 A_1 - \alpha_1 B_1 - \beta_1 A_2 + \alpha_1 B_2 + \beta_2 A_4 - \alpha_2 B_4,\\
\phi_3 A_3 + \theta_3 B_3 &= \alpha_1 B_1 + \beta_1 B_1 + \alpha_1 A_2 + \beta_2 B_2 + \alpha_2 A_4 + \beta_2 B_4,\\
\theta_4 A_4 - \phi_4 B_4 &= \beta_2 A_3 + \alpha_2 B_3,\\
\phi_4 A_4 + \theta_4 B_4 &= -\alpha_2 A_3 + \beta_2 B_3.
\end{aligned}
\tag{18}
$$

From the last four equations in (18) it will be seen that a further simplification can be effected. For A_4 and B_4 are of the order α_2, β_2 in comparison with A_3 and B_3, and the terms $\beta_2 A_4$, $\alpha_2 B_4$, $\alpha_2 A_4$ and $\beta_2 B_4$ on the right-hand side of the fifth and sixth equations in (18) can therefore be neglected in comparison with all other terms involved. We are therefore finally left with six equations only

$$
\begin{aligned}
\theta_1 A_1 - \phi_1 B_1 &= \beta_1 A_3 + \alpha_1 B_3 + \beta_2 A_2 + \alpha_2 B_2,\\
\phi_1 A_1 + \theta_1 B_1 &= -\alpha_1 A_3 + \beta_1 B_3 - \alpha_2 A_2 + \beta_2 B_2,\\
\theta_2 A_2 - \phi_2 B_2 &= \beta_2 A_1 - \alpha_2 B_1 - \beta_1 A_3 + \alpha_1 B_3,\\
\phi_2 A_2 + \theta_2 B_2 &= \alpha_2 A_1 + \beta_2 B_1 + \alpha_1 A_3 + \beta_1 B_3,\\
\theta_3 A_3 - \phi_3 B_3 &= \beta_1 A_1 - \alpha_1 B_1 - \beta_1 A_2 + \alpha_1 B_2,\\
\phi_3 A_3 + \theta_3 B_3 &= \alpha_1 A_1 + \beta_1 B_1 + \alpha_1 A_2 + \beta_1 B_2.
\end{aligned}
\tag{19}
$$

These equations contain only terms having three periodicities, *i. e.*, the principal part of the maintained motion of frequency $(2p_1 + p_2)/2\pi$ and two others, subsidiary to it, which are given by the two nearest admissible points on the periodicity diagram, *i. e.*, of frequencies $(2p - p_2)/2\pi$ and $p_2/2\pi$ respectively. These components are derived from the principal motion by the action on it of the variations in spring, and serve to maintain it permanently in the presence of dissipative forces. They are both small compared with the main motion provided α_1, α_2, β_1, β_2, are small. Fig. 6 represents the vibration curve of this type of summational, and the component of frequency $p_2/2\pi$ (*i. e.*, half that of the graver fork) is very obvious to inspection.

Equations (19) when solved give us values for the five ratios B_1/A_1, B_2/A_1, B_3/A_1, A_2/A_1 and A_3/A_1 and leave us in addition a relation between the "constants" involved in the equations which must be satisfied for steady maintenance to be possible. The solution of the equations by the method of determinants is really a formidable business and is in fact unnecessary: an approximate method of solving them may be used which gives results quite as accurate as the equations themselves. We notice that A_2, B_2, A_3, B_3 are small quantities relatively to A_1, B_1, and further, since k, the coefficient of friction, is necessarily very small for maintenance to be possible, the quantities ϕ_2, ϕ_3 are negligible in comparison with θ_2 and θ_3. The first step in solving the equations (19) is therefore to simplify the last four of them and obtain approximate values for A_2, B_2, A_3, B_3.

We thus have

$$\theta_2 A_2 = \beta_2 A_1 - \alpha_2 B_1 + \frac{1}{\theta_3}\left(\overline{\alpha_1^2 - \beta_1^2} A_1 + 2\alpha_1\beta_1 B_1\right),$$

$$\theta_2 B_2 = \alpha_2 A_1 + \beta_2 B_1 + \frac{1}{\theta_3}\left(2\alpha_1\beta_1 A_1 - \overline{\alpha_1^2 - \beta_1^2} B_1\right),$$

$$\theta_3 A_3 = \beta_1 A_1 - \alpha_1 B_1 + \frac{1}{\theta_2}\left(\overline{\alpha_1\alpha_2 - \beta_1\beta_2} A_1 + \overline{\alpha_1\beta_2 + \alpha_2\beta_1} B_1\right),$$

$$\theta_3 \beta_3 = \alpha_1 A_1 + \beta_1 B_1 + \frac{1}{\theta_2}\left(\overline{\alpha_1\beta_2 + \alpha_2\beta_1} A_1 - \overline{\alpha_1\alpha_2 - \beta_1\beta_2} B_1\right). \qquad (20)$$

The equations give us the values of the subsidiary components of motion in terms of the principal part and of the coefficients of the variable spring by which they are produced.

Substituting these values in the first two of equations (19) we have

$$\theta_1 A_1 + \phi_1 B_1 = \frac{A_1}{\theta_2\theta_3}\Big[\theta_2(\alpha_1^2+\beta_1^2) + \theta_3(\alpha_2^2+\beta_2^2) + 2\beta_2(\alpha_1^2-\beta_1^2) + 4\alpha_2\alpha_1\beta_1\Big]$$
$$+ \frac{B_1}{\theta_2\theta_3}\Big[4\beta_2\alpha_1\beta_1 - 2\alpha_2(\alpha_1^2 - \beta_1^2)\Big],$$

$$\phi_1 A_1 + \theta_1 B_1 = \frac{A_1}{\theta_2\theta_3}\Big[4\beta_2\alpha_1\beta_1 - 2\alpha_2(\alpha_1^2 - \beta_1^2)\Big]$$
$$+ \frac{B_1}{\theta_2\theta_3}\Big[\theta_2(\alpha_1^2+\beta_1^2) + \theta_3(\alpha_2^2+\beta_2^2) - 2\beta_2(\alpha_1^2-\beta_1^2) - 4\alpha_2\alpha_1\beta_1\Big]. \qquad (21)$$

Writing

$$\theta_1 - \frac{1}{\theta_2\theta_3}\Big[\theta_2(\alpha_1^2 + \beta_1^2) + \theta_3(\alpha_2^2 + \beta_2^2)\Big] = \theta,$$

$$\frac{1}{\theta_2\theta_3}\Big[2\beta_2(\alpha_1^2 - \beta_1^2) + 4\alpha_2\alpha_1\beta_1\Big] = a,$$

$$\frac{1}{\theta_2\theta_3}\Big[4\beta_2\alpha_1\beta_1 - 2\alpha_2(\alpha_1^2 - \beta_1^2)\Big] = b,$$

equations (21) may be put into the form

$$(\theta - a)A_1 = (\phi_1 + b)B_1,$$

$$(\theta + a)B_1 = -(\phi_1 - b)A_1. \tag{22}$$

It will be seen that equations (22) are identical in *form* with equations (11) obtained for the summational of the first type and the further discussion must proceed on much the same lines.

The solution is

$$\frac{B_1}{A_1} = \frac{\theta - a}{\phi_1 + b} = \frac{b - \phi}{\theta + a} \tag{23}$$

and the eliminant is

$$\theta^2 - a^2 = b^2 - \phi_1^2. \tag{24}$$

We may as before consider the special case in which $\beta_1 = \beta_2 = 0$ and $\alpha_1 = \alpha_2 = \alpha$

$$\theta_2 A_2 = -\alpha B_1 + \alpha^2 A_1/\theta_3,$$

$$\theta_2 B_2 = \alpha A_1 - \alpha^2 B_1/\theta_3,$$

$$\theta_3 A_3 = -\alpha B_1 + \alpha^2 A_1/\theta_2,$$

$$\theta_3 B_3 = \alpha A_1 - \alpha^2 B_1/\theta_2,$$

$$\frac{B_1}{A_1} = \frac{\theta_1\theta_2\theta_3 - \alpha^2(\theta + \theta_3)}{\phi_1\theta_2\theta_3 - 2\alpha^3} = \frac{-2\alpha^3 - \phi_1\theta_2\theta_3}{\theta_1\theta_2\theta_3 - \alpha^2(\theta_2 + \theta_3)},$$

$$[\theta_1\theta_2\theta_3 - \alpha^2(\theta_2 + \theta_3)]^2 = 4\alpha^6 - \phi_1^2\theta_2^2\theta_3^2. \tag{25}$$

For maintenance to be theoretically possible in this case, the frictional coefficient *k* should be of the third order of small quantities and the adjustment of frequency must therefore be accurate up to the same order.

Cases of summationals of higher orders can be worked out in a similar manner, the approximation being carried to a higher and higher degree as we rise up the series.

THEORY OF DIFFERENTIALS.

The solution of the equation of motion in the case of the first differential is obviously to be obtained in this case by merely writing A_1, B_1, θ_1, ϕ_1 for A_2, B_2, θ_2, ϕ_2 and vice versa, in equations (8) obtained for the summational of the first type. We thus have

$$\theta_1 A_1 - \phi_1 B_1 = A_2(\beta_2 - \beta_1) + B_2(\alpha_1 - \alpha_2),$$

$$\phi_1 A_1 + \theta_1 B_1 = A_2(\alpha_1 + \alpha_2) + B_2(\beta_1 + \beta_2),$$

$$\theta_2 A_2 - \phi_2 B_2 = A_1(\beta_2 - \beta_1) + B_1(\alpha_1 + \alpha_2),$$

$$\phi_2 A_2 + \theta_2 B_2 = A_1(\alpha_1 - \alpha_2) + B_1(\beta_1 + \beta_2), \tag{26}$$

where

$$U = A_1 \sin(p_1 - p_2)t + B_1 \cos(p_1 - p_2)t$$
$$+ A_2 \sin(p_1 + p_2)t + B_2 \cos(p_1 - p_2)t + \text{etc.} \quad (27)$$

and

$$\theta_1 = n^2 - \overline{p_1 - p_2}^2, \quad \theta_2 = n^2 - \overline{p_1 + p_2}^2,$$
$$\phi_1 = k(p_1 - p_2) \text{ and } \phi_2 = k(p_1 + p_2).$$

Proceeding as before, we put

$$\begin{aligned} \theta_2 A_2 &= A_1(\beta_2 - \beta_1) + B_1(\alpha_1 + \alpha_2), \\ \theta_2 B_2 &= A_1(\alpha_1 - \alpha_2) + B_1(\beta_1 + \beta_2), \end{aligned} \quad (28)$$

$$\theta_1 A_1 - \phi_1 B_1 = \frac{A_1}{\theta_1}\Big[(\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2) - 2(\alpha_1\alpha_2 + \beta_1\beta_2)\Big]$$
$$+ \frac{B_1}{\theta_2}\Big[2(\alpha_1\beta_2 - \alpha_2\beta_1)\Big],$$

$$\phi_1 A_1 + \theta_1 B_1 = \frac{A_1}{\theta_2}\Big[2(\alpha_1\beta_2 - \alpha_2\beta_1)\Big]$$
$$+ \frac{B_1}{\theta_2}\Big[(\alpha_1^2 + \beta_1^2) + (\alpha_2^2 + \beta_2^2) + 2(\alpha_1\alpha_2 + \beta_1\beta_2)\Big]. \quad (29)$$

It will be seen that equations (29) are of the same general form as (10) with certain modifications. The terms on the right-hand sides of (10) and (29) can be derived from each other by writing α_2 for $-\alpha_2$ and vice versa. The further reduction of equations (29) may be proceeded with in the usual way.

The outstanding feature of the differential types is the relative difficulty of isolating and maintaining them successfully. No doubt this is partly due to the fact that the differentials of any given order are of much lower frequency than the summationals of the same order, and they lie therefore generally in the very region of frequencies in which simpler types of resonance are maintained far more powerfully over wide ranges. These latter are maintained by preference and extinguish the differentials. The foregoing however does not appear to be a complete explanation. Possibly the following further considerations must also be taken into account in explaining the relative poverty of differentials. In the mathematical discussion, it was shown that the subsidiary components of motion introduced under the action of the variable spring, themselves enabled the principal motion to be maintained, and the relative amplitudes and phases of these components were determined on the assumption that n^2, the free spring of the system, was a constant. It was however indicated that in practice this was not strictly the case, and in fact the success or otherwise of the experiments, *i. e.*, the steady maintenance of vibration in a certain amplitude, is dependent on the quantity n^2 not being itself absolutely a constant. For large displacements n^2 is greater than for small displacements and the equation of motion when modified to take account of this fact may be written thus,

$$\ddot{U} + k\dot{U} + [n^2 + mU^2 - \overline{2\alpha_1 \sin 2p_1t + \beta_1 \cos 2p_1t} - \overline{2\alpha_2 \sin 2p_2t + \beta_2 \cos 2p_2t}]U = 0. \quad (30)$$

The quantity mU^2 has been added to the third term within the brackets to represent the increase of spring for large displacements in a *symmetrical* system. It is obvious that when expanded for any periodic solution of U, mU^2 will give us both constant and periodic terms. The latter, *i. e.*, the periodic terms, would be of various frequencies, and of them the most important would be those which are sines or cosines of $2p_1t$ or $2p_2t$, since they would directly modify the action of the components of the variable spring. It is therefore quite evident that the amplitudes and phases of the subsidiary components of motion would not be the same as when mU^2 is omitted. Some components would tend to increase at the expense of others. Instances of such action have already been furnished in my previous publications when discussing maintenance by a simple variation of spring.

What we may expect to find is that when mU^2 is taken into account in the equation of motion, the subsidiary components which maintain differentials are less effective than they would otherwise be, whereas, in the case of summationals, they would be more effective. For, in the former case, some of them at least are of frequency higher than that of the maintained motion, in the latter they are invariably less, and the components of lower frequencies are encouraged at the expense of those of higher frequencies.

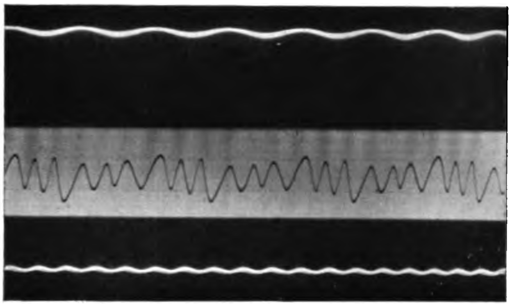

FIG. 6.

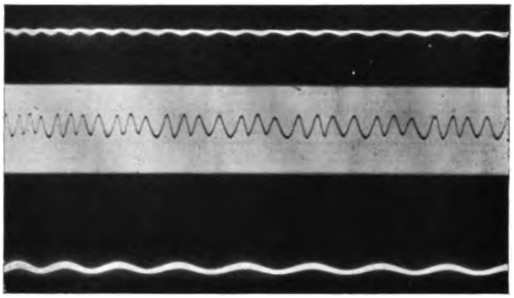

FIG. 7.

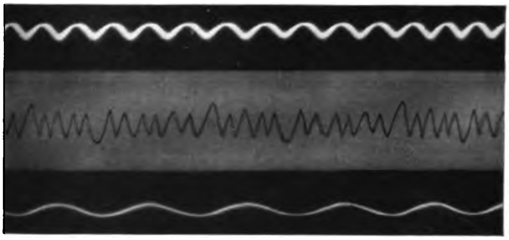

FIG. 8.

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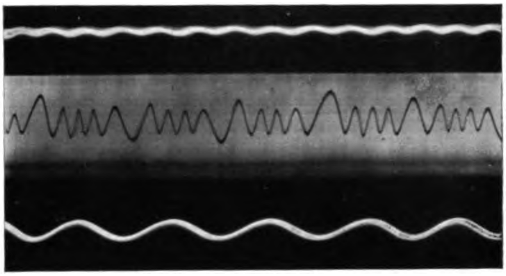

FIG. 9.

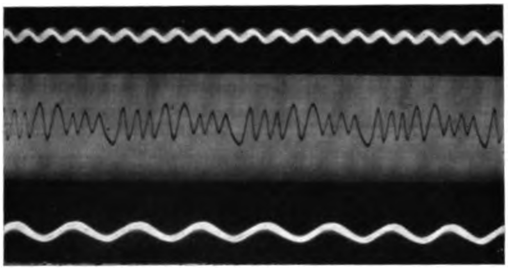

FIG. 10.

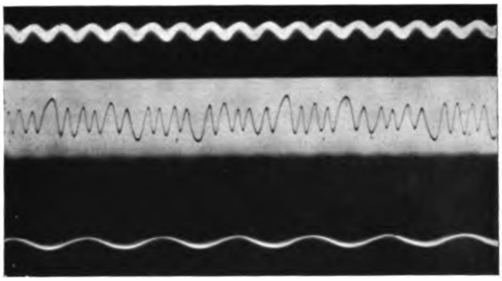

FIG. 11.

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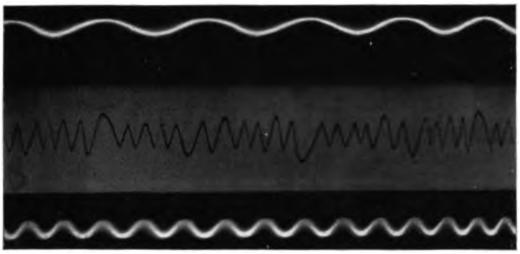

FIG. 12.

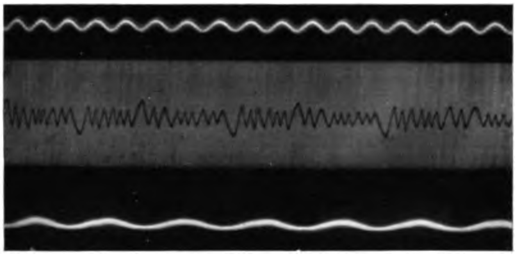

FIG. 13.

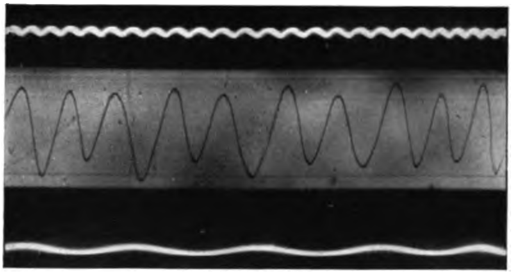

FIG. 14.

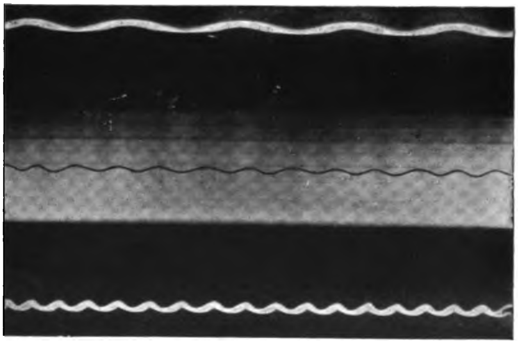

FIG. 15.

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RESISTANCE OF CARBON CONTACTS IN THE SOLID BACK TRANSMITTER.

By A. L. Clark.

IN a previous paper,[1] I have described experiments which show the time relations of resistance of carbon contacts. The following paper describes the application of the work of the first paper to some phenomena observed in ordinary solid back telephone transmitters, and continues the work of the previous paper.

While it seems hardly possible that the phenomena described below have escaped notice, no account of them has been discovered in the available literature. That the resistance of such transmitters varies with the time and applied electromotive force has been known ever since such transmitters have been used, but the cause of these variations as well as their astonishing regularity have not been adequately discussed—at least not to the knowledge of the writer. They are generally regarded as of a more or less erratic and uncertain character.

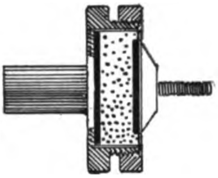

Fig. 1.

The essentials of transmitter of the so-called solid back type, with diaphragm and mouth-piece omitted, are shown in Fig. 1. The instrument consists of a cylindrical brass capsule, having one end closed and the other open. The cylindrical wall is covered inside with a thin layer of insulating material (usually paper), and the bottom is covered with a disk of carbon securely attached to the brass end of the capsule. The other end of the capsule is covered with a second carbon disk, mounted on a thin mica plate and held in place by a brass ring which is screwed on to the barrel of the capsule so that it bites the edge of the mica plate. The capsule is nearly full of carbon grains, which close the electrical circuit between the two carbon disks. The mica mounted disk is attached to the diaphragm of the transmitter and vibrates with it, when it is acted upon by sound waves, and thus alternately compresses and releases the carbon grains. The changes in contact pressure thus produced cause great changes in the electrical resistance of the system, resulting in the variations of current strength necessary for the transmission of sounds in practical telephony.

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[1] Physical Review (2), I., 50, 1913.

If a solid back transmitter whose front disk is given sufficient elastic freedom of motion, is placed in an electrical circuit where the potential difference between its plates is a few volts, the following phenomena are observed. The resistance rises at first—in some cases as much as 100 per cent. or more—and then falls off more slowly. The rapidity of the rise in the earlier part of the experiment as well as the amount of rise, and later, the rapidity of the fall in resistance depend on the current density through the apparatus, being greater for large currents than for small. Fig. 2 shows the changes in resistance with time. It will be seen that the initial value of the resistance is largely a matter of accident, depending on the arrangement of the grains and the pressure with which they are held together. The time is given in seconds and the resistance in ohms. This is true for all the curves showing time relations.

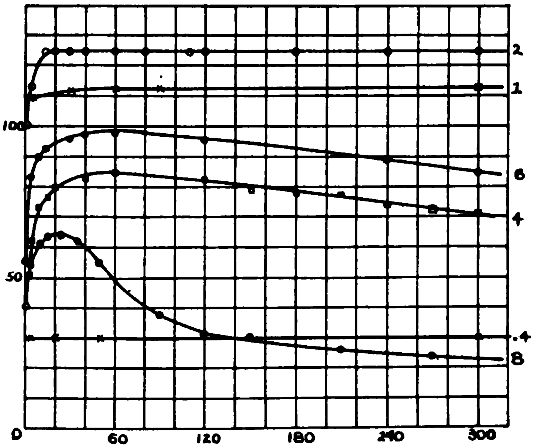

Fig. 2.

The explanation of the phenomena observed above is as follows: In the upper part of the transmitter, the current passes between points in loose contact[1] while in the lower part the contacts are tight. According to the results of my previous experiments the resistance of the contacts in the upper part of the capsule is increased when the current passes, while in the lower part there is very little change. Consequently, when the current is first turned on, the resistance rises; but after a certain time the heating of the granules causes increased pressure and shifting of points of contact which reduces the resistance again. No doubt a part of this later decrease is due to the fact that the temperature coefficient of carbon is negative. Thus we have two causes operating together; viz. the increase due to the loose contact effect and the increase of pressure

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[1] Loc. cit.

due to expansion. The former predominates at first, but is overtaken by the latter. If the transmitter be jarred during the observation (see Fig. 11), the resistance drops back to nearly its initial value and the changes in resistance occur over again. This will be discussed again later on.

The phenomena have an additional complication when the carbon granules are enclosed in a capsule all of whose walls are rigid. This rigidity may be effected by clamping so that the front mica disk is held firmly, or this disk may be held with wax. In this case the points of contact which are suddenly heated by the current, expand, causing an increase in pressure between the grains, giving rise to a rapid decrease in resistance. This initial rise is soon overtaken by the increase of loose contact resistance which in turn is overtaken by the expansion due to the general rise in temperature (see Fig. 3). The initial decrease in resistance which appears when the ends of the capsules are rigidly held is seldom noticed in the ordinary use of the transmitter, because the elasticity of the mica plate holding the front carbon disk, does not allow the pressure to increase so rapidly. In other words, in the ordinary use of the transmitter, the loose contact resistance *increases* so much more rapidly than the *decrease* due to the expansion of the points, that the resistance rises instead of falls. Fig. 3 shows the manner in which the resistance changes when both disks are rigidly held. Occasionally, even in the ordinary use of the transmitter, where the mica mounting is not sufficiently elastic, there is a trace of the initial decrease.

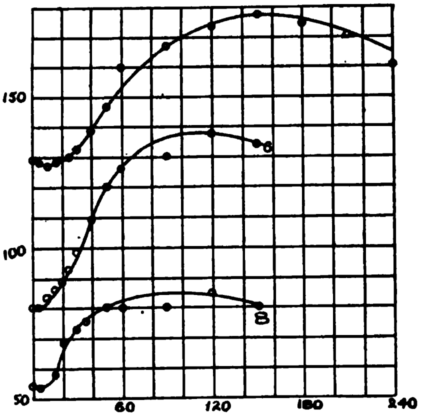

Fig. 3.

The method employed in the measurement of the resistance was a simple ammeter-voltmeter method, with dead-beat instruments which were read at short intervals. The transmitter was connected directly to a storage battery so that the applied E.M.F. remained constant.

That the sudden expansion of the grains mentioned above actually occurs was shown by the following experiment. The capsule was rigidly mounted in a clamp so that as a whole it was immovable and an optical lever with a very short arm was attached to the front disk. The current was turned on and the expansion noted with a telescope and scale. The system was arranged so that the magnification was about one thousand.

Fig. 4 shows the expansion with the time. The ordinates are thousandths of millimeters.

It will be noticed that the expansion is most rapid at the beginning and appears soon enough to make the explanation of the initial drop in the curves of Fig. 3 acceptable.

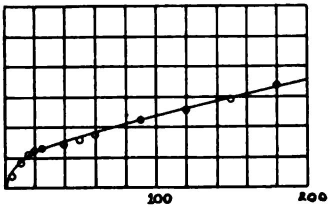

Fig. 4.

Whether we will have the curves of Fig. 2 or 3, depends upon the rigidity of the support of the carbon disk. If the rigidity is not too great, the increase in pressure is not great enough to give a droop to the curve. If the rigidity is increased, the increase in resistance may not be rapid enough to overcome the tendency to droop, so occasionally we find a transmitter where the droop sometimes appears, and sometimes does not.

When very coarse grains are used the influence of individual contacts becomes so marked that accurate readings of current cannot be taken. Occasionally with very coarse grains such as number 16, the resistance rises rapidly to a very high value which shows that in such a case the majority of the contacts are loose. With grains as fine as number 80, the effect observed is statistical and no trouble is experienced in the readings. The grains and disks used in these experiments were obtained from the Canadian National Carbon Company, which kindly furnished grains of various sizes as well as disks with different degrees of polish.

To return to the curve of Fig. 2. That the explanation of the initial rise in resistance is correct was shown as follows: A capsule was made of a hollow brass cylinder and a carbon disk stuck on to the back with sealing wax insulating it from the brass, and the front was covered with the ordinary mica-mounted disk. A stiff copper wire *P* (see Fig. 5) was soldered to the middle of this disk to convey the current and small wires *M* and *N* soldered to its top and bottom. These last wires were connected to a galvanometer through a resistance box. This box was placed in the circuit to control the deflection of the galvanometer.

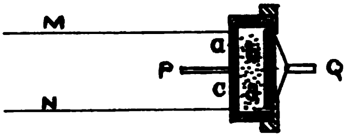

Fig. 5.

Thus the galvanometer may be used to measure the P.D. between top and bottom of the disk to which they are connected. A battery and ammeter were connected to *P* and *Q*.

It will be seen from the diagram of connections that we have virtually a Wheatstone Bridge arrangement. Let *abcd* refer to the various parts of the net representing in each case the resistance of the part on which the letter is found. The upper and lower parts of the larger disk of the capsule, *a* and *c* are divided from each other by the leading wire. The upper and lower parts of the carbon grains *b* and *d* are divided at the same place. The front disk of the capsule takes the current from all over its face and the resistance of the brass conducting layer is too small to be taken into consideration.

Let E be the constant applied E.M.F. between P and Q, I the total current measured by the ammeter, and V the potential difference between the top and bottom of the fixed carbon disk, shown by the galvanometer. The problem is to determine how the resistance of b and d affect the values of I and V (actually I/V).

Now

$$i_{ab} = \frac{E}{a+b} \text{ and } i_{cd} = \frac{E}{c+d}$$

So

$$I = i_{ab} + i_{cd} = E\left(\frac{a+b+c+d}{(a+b)(c+d)}\right).$$

The drops in potential on a and c are

$$V_a = \frac{Ea}{a+b},\ V_c = \frac{Ec}{c+d} \text{ and } V_a - V_c = V = E\left(\frac{a}{a+b} - \frac{c}{c+d}\right)$$

so finally

$$\frac{I}{V} = \frac{a+b+c+d}{ad-bc}.$$

Now if $a/c < b/d$ the current is from ab to cd or down on the figure. If $(a/c) > (b/d)$ the current is up.

In general b is larger than d, while a and c are nearly equal, so that if the capsule is turned over, d becomes larger than b and the current in the galvanometer is reversed. If a and c are unequal the current may not reverse.

Now $\dfrac{\partial(I/V)}{\partial b} = \dfrac{ad+ac+c^2+cd}{(ad-bc)^2}$ which is always positive, or an increase in the value of b causes an increase in I/V.

In the same way

$$\frac{\partial(I/V)}{\partial d} = -\frac{c+bd+cd+d^2}{(ad-bc)^2}$$

which is always negative or an increase in d causes a decrease in the value of I/V. Fig. 6 shows the way in which I/V changes with the time. It will be noticed that I/V increases to a maximum and then diminishes.

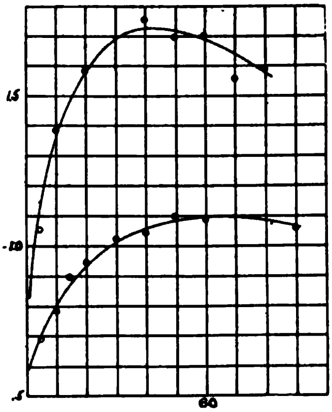

Fig. 6.

So the initial rise in the value of I/V is due to either an increase in b or a decrease in d. If due to the latter I should increase also, which is not the case. So the first change in I/V must be due to an increase in b or the loose contact effect in the upper half of the transmitter.

The decline in I/V after the maximum value is due to either a decrease in b or an increase in d, if due to the former it is caused no doubt by crowding of the grains with shifting, thus presenting new points of contact. If the decrease in I/V is due to an increase in d, it is caused by the loose contact effect extending into the lower part of the transmitter. Probably the latter cause operates first as the current does not begin to rise until after the maximum in I/V. The inequality of a and c are brought out in the two curves of Fig. 6. They represent the value of I/V for the two positions of the transmitter.

Fig. 7 shows the effect on the resistance due to changing the E.M.F. from 2 to 4 volts and back again. The two sets of curves, which can be distinguished easily, are for changes after long and short runs respectively. It will be noticed that an increase in current is always followed by an increase in resistance and a decrease in current by decrease in resistance. The reason for the decrease in resistance is probably due to the shifting of the grains with the falling temperature. It has been proved beyond all question that a very slight change only in the position of contacts on the grains is necessary for restoration of the initial conductivity after the loose contact effect has occurred.

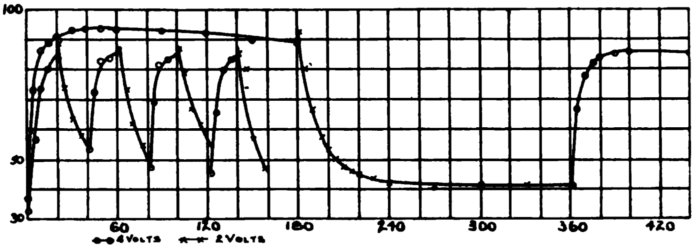

Fig. 7.

The recovery of the transmitter after a run was investigated as follows:

The exciting current was passed through the transmitter for a definite interval and then broken, and the circuit completed again with an exceedingly small current passed through the transmitter in series with a low range milammeter. A double-pole commutator made it possible to connect the transmitter in either circuit at will without loss of time. A resistance box was afterwards substituted for the transmitter and the readings of the milammeter reduced to ohms by substitution. Curve 1 of Fig. 2 shows that the resistance of a transmitter is practically constant when a very weak current is sent through it; so this method is applicable. Of course, the actual resistance of the transmitter depends on the current so that the value of the resistance measured with a small current is not the same as when the current is larger. However, the changes in resistance can be followed perfectly satisfactorily. Fig. 8 shows two sets of curves. These curves are of long and short runs. In the case of a system of carbon grains, enclosed in a capsule with rigid walls or in an ordinary transmitter capsule where the front disk is clamped or fastened in any other way, the recovery after a run is somewhat different. The resistance rises rapidly at first and then falls off as in the case just explained. No doubt this is due to the release of the pressure due to contraction attending the rapid cooling of the points of contact.

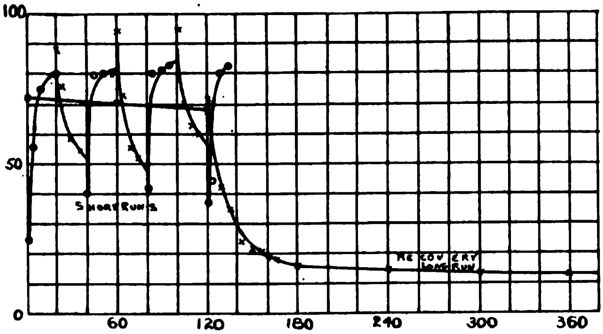

Fig. 8.

If the pressure on the grains be increased in any way, such as by pressing on the mica-mounted disk, the resistance of the transmitter falls but quickly begins to rise again owing to the increased current. If the pressure be released, the resistance always rises but falls again immediately (see Fig. 9). The pressure was applied by pressing on the diaphragm of the transmitter with a small bristle brush.

So we see that an ordinary solid back transmitter as commonly used is a partially conservative system, as far as its resistance is concerned. Anything which causes an increase in current is met by an increase in resistance which cuts down the current; while if the current be decreased in any way the resistance decreases, causing an increase of the current.

The question, whether or not the changes in resistance which occur with increase or decrease of pressure on the diaphragm take place quickly enough to affect the wave form when the transmitter is used in ordinary telephony, was examined, with the result that except possibly for sounds of very low pitch there can be little or no distortion due to the kind of changes just mentioned. The method employed in deciding this point was as follows: A small car on well-made wheels was arranged to run down an incline on a smooth track, dragging a brass spring brush on one of the rails, which was covered with paper, except for a small interval near the lower end. In this way the car made a momentary contact with the rail which allowed the current to pass through the transmitter for a brief interval. This interval could be varied by changing the inclination of the track. The length of the interval was determined by switching the current through the pen circuit of a drum chronograph. After the passage of the momentary current, the resistance of the transmitter was measured as in the experiment on recovery. The procedure was as follows: The resistance was first measured using the small current.

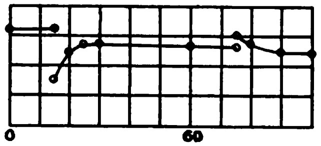

Fig. 9.

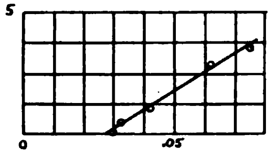

Fig. 10.

Next the car was allowed to run down making the contact through the transmitter, then allowed to run down making the same contact for the chronograph, and finally the resistance of the transmitter measured again. These operations were repeated for various inclinations. The results are shown in Fig. 10. The ordinates show increase in resistance in tenths of ohms. It will be noticed that the curve crosses the axis at about .03 seconds, which is the longest time for which no change in resistance could be noted. In all probability this curve is tangent to the horizontal axis at the origin but no measurable change in resistance occurred for a time less than .03 seconds. Thus we may conclude that the effect on the wave form is probably of no importance. Fig. 11 shows the effect of jarring the transmitter during the run as well as during the recovery.

There is no evidence of a secular change in resistance when the transmitter is used continuously over a long interval of time. On the contrary, an experiment carried out for several days showed no sure change in resistance. A circuit breaker was arranged to make the current for 10 seconds once every minute and at the end of 48 hours the resistance curve was almost identical with the curve at the beginning of the experiment.

That the gas in which the transmitter grains are placed exercises a marked effect on their contact resistance is shown by the following experiment. A transmitter capsule with a number of small orifices in the brass back and grooves in the back of the carbon disk to allow circulation of the gas, was placed in a receiver from which the gas could be removed by pump. With air in the receiver the resistance curves were those of Fig. 2. Also see Curve 1, Fig. 13. When the air was pumped out the curves became like those of Fig. 3 (Curve 2, Fig. 13). When the air is removed so that the pressure is about 3 mm. the rise in resistance due to the loose contact effect is very small and the droop in the curve due to the sudden expansion becomes noticeable. As soon as the air was re-admitted the curve went back to the Curve 1 class. In some of the trials the apparatus stood for several hours before measurements were taken in order that there should be no doubt that the air pressure inside the capsule was the same as the pressure in the receiver. Fig. 12 shows the relation between the resistance of a transmitter and the air pressure. One thing that should be noticed is that at any given pressure the resistance is decreased by the passage of current which indicates that the escape of the air is facilitated by the heat generated at the points of contact. This effect was noticed in the previous experiments on carbon resistance.

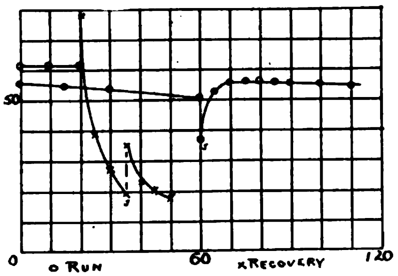

Fig. 11.

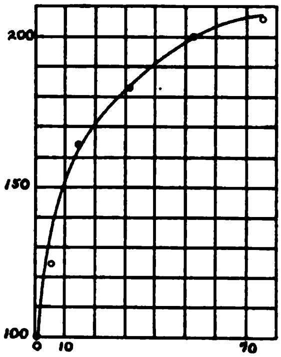

Fig. 12.

The effect of filling the receiver with oxygen is suggestive. When the transmitter is filled with oxygen the resistance curve rises with much greater rapidity and much higher than when it is filled with air and there is no trace of the droop in the curve shown in Fig. 3. Here the resistance increases so rapidly that the inclination is much sharper than with air. This supports the suggestion made in the previous paper that the rise in resistance, in part at least, may be due to actual combustion with the formation of an ash or other material of permanently high resistance. Curve 3, Fig. 13 shows the resistance of an oxygen-filled transmitter. These experiments indicate that the gas at points of contact exercises more influence than usually believed.

Thus far the work described has been on a transmitter which is kept perfectly quiet. The effect of a sound on the resistance of the transmitter is interesting. An ordinary central station instrument whose capsule is exactly like those employed in the previous experiments, was used. This was suspended on spiral spring leading wires so that it was free from jar. The sound was produced by an organ pipe (256 vibrations) near the mouth-piece of the transmitter. The phenomena exhibited by this instrument differ very little from those already described with a quiet transmitter, except that the changes in resistance are much less as would be expected. One interesting result was noted which shows again the conservative action of the transmitter. When the sound is turned on, the resistance of the transmitter is increased, due no doubt to the loosening effect of the vibration, but the resistance begins to decrease immediately. If the lip of the pipe is covered to stop the sound, but to leave other conditions unchanged, the resistance falls immediately but presently starts to rise again.

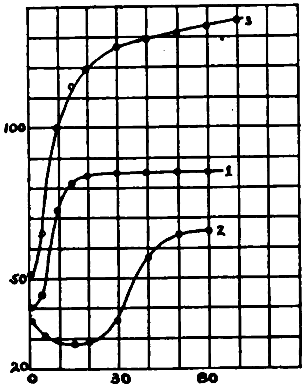

Fig. 13.

The results of the foregoing experiments indicate that the theory of the action of the transmitter is not complete and that more than area of contact must be taken into account to explain the changes in resistance. The action of the gas is certainly of importance. A further study of the effect of various conditions discussed above on the wave form has been begun and the results will be published in a future paper.

NOTES ON ELECTRODE AND DIFFUSION POTENTIALS.

By G. W. Moffitt.

In a recent paper[1] the writer has shown that the differences of potential between liquid surfaces and the air above them may be considerably greater than had usually been supposed. In some cases the value of this contact potential difference was changed as much as three tenths of a volt by slightly contaminating the surface of the liquid. It was also found that the value of this contact potential difference for clean fresh liquid surfaces is a steady value,—at least within a few thousandths of a volt,—and it is probable that the small variations in the observed values are due to the difficulties entering into the experiment.

It seems quite reasonable to assume then that there exists at the clean bounding surface of a liquid and air a definite difference of potential. The value of this potential in certain cases may be zero.

J. J. Thomson's work[2] on the electricity of drops points to the same conclusion from entirely different experimental evidence, as does some recent work by McTaggart.[3] Thomson found that certain solutions—zinc chloride in water for example—in contact with air seem to show no electrification after the concentration has reached a certain value. McTaggart observed the motion of small air bubbles through liquids in which an electrostatic field was maintained. The bubbles were held in the axis of a horizontal glass tube filled with the liquid by the rapid rotation of the tube on its axis. The bubbles were free to move with or against the field which was parallel to the axis of the tube. He points out that the electrification set free by a falling drop is less than the charge as computed from the surface density and the area of the drop surface, and considers this last charge as the one effective in static, cataphoresis experiments. This means that only a part of the charge on a drop is set free by being broken up in air or by striking an obstacle. This would be expected. We would expect, however, that a drop neutral in the static condition would be neutral also when falling or when striking an obstacle. For the purposes of the present paper we may neglect any possible effects due to differences of concentration in the

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[1] Phys. Rev., N. S., Vol. II., No. 2, Aug., 1913.

[2] Phil. Mag., Ser. V., Vol. 37, p. 341, 1894.

[3] Phil. Mag., Ser. VI., Vol. 27, p. 297, 1914.

surface film for results referred to later show that the neutral condition of the drop prevails throughout great variation of concentration. These views are supported by the few instances where data by the two methods can be compared. It may also be pointed out that in the cataphoresis experiments the liquid surface is sharply concave while with splashing drops it is either irregular or sharply convex. In view of these facts it seems reasonable to assume that conditions of electrical neutrality are the same for drops as for a clean level surface of the same liquid, and that solutions may be selected by the falling drop method whose air-liquid potential differences are negligibly small.

In the writer's work mentioned above values of the diffusion potential plus the difference of the two air-liquid potential differences were given for various solutions. If the solutions used had been those found by Thomson to exhibit no electrification in air we should have had values of the diffusion potentials for those particular cases. We have then a method of measuring potential differences between solutions in certain cases which is independent of theoretical assumptions. For instance, the diffusion potentials of zinc chloride solutions may be measured for concentrations greater than those for which the solution pressure theory seems to hold,—as determined by measurement of the electromotive force of concentration cells. It is by no means evident that an electrode potential for an electrode in an aqueous solution of an electrode salt can be computed in many cases, and diffusion potentials determined in this way seem likely to be in error. Especially is this true for the more concentrated solutions. In the case where the dissolved substance does not contain the element of which the electrode is composed we are still more uncertain. It seems therefore, that a direct method, tedious and inaccurate as it may be, would lead to results worth while.

On looking over Thomson's data on the electrification due to the splashing of drops no results were found for the solutions used by the writer in the work referred to above. It was decided to set up an apparatus similar in principle to that used by Thomson, and study the air-liquid surface potential differences for these solutions. A sensitive Dolazalek electrometer was used to detect the presence of the charges. One pair of quadrants was earthed, and the other was connected by means of a small copper wire to the solution in an insulated glass funnel from which the drops fell on a brass plate elevated from the bottom of a brass vessel in which the solution accumulated after splashing. This brass vessel was also insulated from the earth and connected to the insulated quadrants. Instead of using a fan to remove the charged air from the vicinity of the splashing drops a piece of brass tubing, flattened at one end somewhat like a fishtail burner, was placed in a horizontal position on a line just above the plate on which the drops fell, and a few inches from the side of the brass vessel. This tube was connected to the compressed air supply and a gentle, steady stream of air kept passing over the vessel. The apparatus was frequently tested during the experiments for leakage and spurious charging effects by placing everything in position and observing the action of the electrometer when the solution was not dripping from the funnel. At times a slight positive charging was noted and wherever it appeared correction has been made for it in the results given below.

Distilled water was tried and a positive charge accumulated quite rapidly. A normal solution of sodium chloride was next tried and no charging resulted. Another portion of the solution was watered up to 0.5 normal. This produced no charging effect. Nor did a 0.1 normal solution prepared in the same way. A little distilled water was then run through the funnel to clean it and then the positive charging due to water was again observed. This is an example of the procedure in all cases distilled water being used before and after each series of solutions. In a similar manner solutions of sodium bromide, sodium sulphate, copper sulphate, and copper chloride were tried. All these were neutral in air at concentrations ranging from normal to less than tenth normal. Since the object of the experiment was to determine whether these solutions were neutral to air throughout this range of concentration no pains were taken to accurately measure the concentration.

These results show that the values published by the writer in Physical Review, page 106, 1913, are, except in the case of zero concentration, the sum of the constant plate surface potential plus the liquid-metal potential difference in each case, and that the results on page 107 are the values of the diffusion potential differences for the solutions named.

Further, the effect of the anion on an electrode potential has been the subject of considerable discussion. It is generally looked upon as having little to do with the value of an electrode potential in the case where the cation is the same as the electrode. The variations in the two $ML + K$ curves for copper sulphate are probably due to uncontrolled factors. The two curves for sodium chloride also show some irregularities. The curve for sodium bromide lies close to the chloride curves, indicating that there is not much difference in the effects of these two anions on the electrode potential. The sodium sulphate curve, however, is removed from the other sodium curves, indicating that the sulphate ion has a different effect on the electrode potential than the halogen ions have. In these examples the cation is not the same as the electrode.

Why the anion should not affect the electrode potential is not clear. It seems more reasonable in the light of such cases as that just mentioned, to assume that in general the anion probably does exert some influence and that for the dilute solutions employed in concentration cells the effect at one electrode may be very nearly balanced by the oppositely directed effect at the other.

STATE UNIVERSITY OF IOWA,
September, 1914.

THE LEDUC EFFECT IN SOME METALS AND ALLOYS.

By Alpheus W. Smith and Alva W. Smith.

If a metal plate having a longitudinal flow of heat in it is placed in a magnetic field which is perpendicular to the plane of the plate, a transverse difference of temperature is observed. This effect may be described as a rotation of the isothermal by the magnetic field and is known as the Leduc effect. This transverse difference of temperature $\Delta\theta$ will be determined by the width of the plate w, the longitudinal temperature gradient $\partial T/\partial x$, the magnetic field H and the nature of the plate. The coefficent of the Leduc effect ${}_hT_h$ is given by the equation,

$$\Delta\theta = {}_hT_h\, wH \cdot \frac{\partial T}{\partial x}.$$

According to the notation of Hall and Campbell[1] which is being followed, the T calls attention to the fact that the observed effect is at right angles to the longitudinal flow of heat; the subscript h preceding T indicates that the longitudinal flow is thermal and the other subscript h indicates that the transverse effect is thermal. Fig. 1 shows the accepted convention as to the sign of the coefficient. The rectangle represents the metal plate to be investigated; the arrows at either end of the plate, the direction of the longitudinal heat current and the arrows on the circle, the direction of the magnetizing current. If the rotation of the isothermal is in the direction in which the magnetizing current flows, the coefficient ${}_hT_h$ is said to be positive.

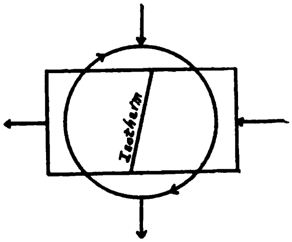

Fig. 1.

The plates used for this investigation were about 3 cm. long, 1.7 cm. wide and 1 or 2 mm. thick. In Fig. 2 is shown a plate with the copper-advance thermal couples attached for measuring the longitudinal temperature gradient and the transverse change of temperature. The longitudinal thermal couples C and D were soldered to the surface of the plate; the transverse ones A and B were imbedded in the edges of the plate and held in position by as small amount of solder as possible. The thermal junctions which were not soldered to the plate were in each case

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[1] Proc. Am. Acad. of Arts and Sci., 46, p. 625 (1911).

immersed in a constant temperature-bath which was kept at room temperature. The thermoelectric heights of these thermal couples were determined over the range of temperature used in these experiments. The plate was soldered to copper projections from two rigidly connected copper tubes. Through one of these tubes flowed water at room temperature; through the other, steam. The plate was enclosed in a thin box of hard rubber or black fibre and the box was filled with magnesia oxide. The plate was then rigidly mounted between the poles of the electromagnet.

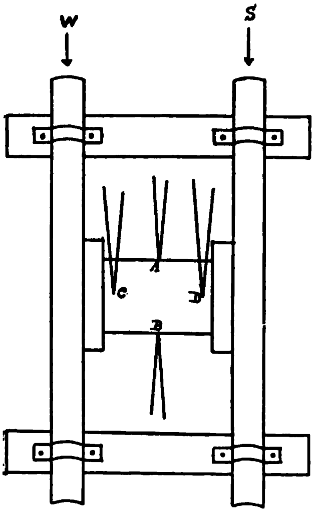

Fig. 2.

The couples with which the longitudinal temperature gradient was determined were used in the usual manner with a slide-wire potentiometer. The transverse temperature difference set up by the magnetic action was determined by connecting the thermal couples which were connected to the opposite sides of the plate, differentially to the coils of a Broca galvanometer. Since these couples could not be located exactly on the same isothermal, the galvanometer would in general show a deflection before the magnetic field was established. In order to compensate for any such inequality of thermoelectromotive forces tending to give a deflection of the galvanometer a slide-wire potentiometer was arranged in series with one of the coils of the galvanometer so that any electromotive force necessary to bring the galvanometer needle to its zero position could be introduced. The magnet was placed about 30 feet from the galvanometer and so oriented that the excitation of magnet produced less than a millimeter deflection in the galvanometer on open circuit. With the plate in position between the poles of the magnet a steady stream of water at room temperature was passed through one of the copper tubes and steam, through the other. When the flow of heat had become steady, the galvanometer circuit was closed and the slider on the potentiometer was adjusted so that the galvanometer showed no deflection. With the galvanometer circuit open the magnetic field was established. As soon as conditions of equilibrium had been reached, the deflection of the galvanometer corresponding to the change of temperature at the edges of the plate was noted. The observations were repeated with the magnetic field reversed. The mean of these observations was taken as the deflection corresponding to the change of temperature due to the magnetic action. Three or more such sets of observations were taken for each magnetic field. From the average of these deflections, the sensibility of the galvanometer and the thermoelectric height of the thermal couple the transverse change of temperature between the edges of the plate was calculated. The mean of the temperatures of the ends of the plate was taken as the temperature of the middle of the plate and, therefore, the temperature at which the Leduc coefficient was determined. The deflection increased for nearly a minute after the excitation of the magnet. The readings were taken when a constant deflection had been reached. The sensibility of the galvanometer which for a fixed scale distance of about 200 cm. amounted to about 5×10^{-7} volts per cm. was taken for each series of observations.

In Table I. are given the results for nickel, nichrome, electrolytic iron and cobalt. The nickel and cobalt were obtained from Kahlbaum. The electrolytic iron was kindly furnished by Professor Burgess, of the University of Wisconsin. It has been shown that this iron is very free from impurities. In Table I. T is the temperature at the middle of

Table I.

Nichrome, $T = 56.9°$.		Nickel, $T = 61°$.	
H	$\frac{\Delta\theta}{w} + \frac{\partial T}{\partial x}$.	H	$\frac{\Delta\theta}{w} \div \frac{\partial T}{\partial x}$.
2,130	16.7×10^{-4}	2,340	34.9×10^{-4}
4,320	33.6	4,300	58.6
6,550	39.0	6,320	66.4
7,970	41.9	8,500	67.3
9,120	41.9	10,880	68.9
9,820	41.9		
10,800	41.9		

Electrolytic Iron, $T = 56.9°$.		Cobalt, $T = 53.7°$.	
H	$\frac{\Delta\theta}{w} + \frac{\partial T}{\partial x}$.	H	$\frac{\Delta\theta}{w} + \frac{\partial T}{\partial x}$.
4,284	18.1×10^{-4}	4,200	29.2×10^{-4}
6,650	27.5	6,600	44.3
8,200	34.4	8,000	52.4
11,900	46.7	11,800	75.6
15,800	62.9	15,800	86.4
18,900	74.6	18,900	86.5
21,400	79.0	21,400	86.4
23,100	81.2		

the plate where the effect was observed; H is the magnetic field in gausses; $(\Delta\theta/w) \div (\partial T/\partial x)$ gives the transverse change of temperature in degrees Centigrade for a plate one centimeter wide with a longitudinal temperature gradient of one degree Centigrade per centimeter in it. These results are also shown graphically in Fig. 3, where field strengths in gausses have been plotted as abscissæ and $(\Delta\theta/w) \div (\partial T/\partial x)$ as ordinates. It will be observed that the Leduc effect in nickel is opposite to that in iron, cobalt and nichrome. For lower magnetic fields the effect is nearly proportional to the intensity of the magnetic field. For sufficiently high magnetic fields the difference of temperature set up by the magnetic action approaches a constant value. The curves showing the dependence of the Leduc effect on the magnetic field are exactly like those showing the dependence of the Hall effect and the Nernst effect on the magnetic field. In each of these three cases the effect is proportional to the

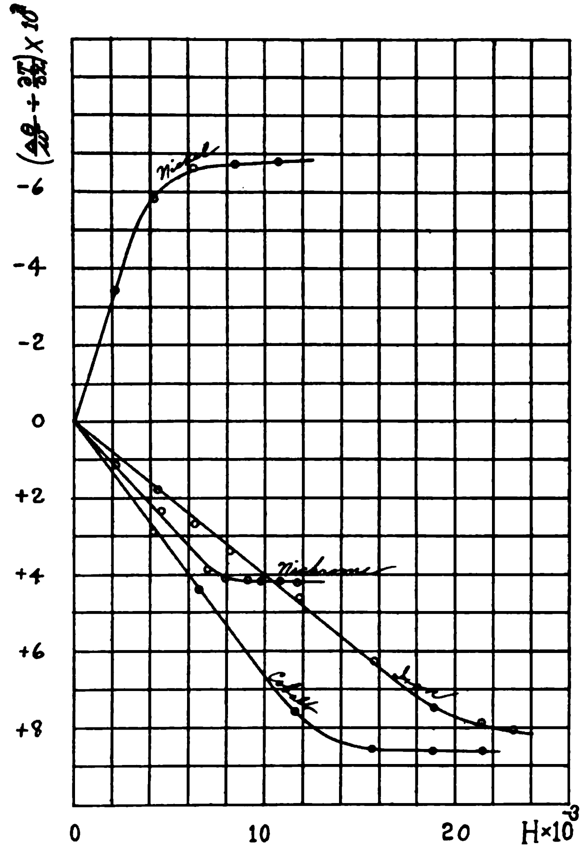

Fig. 3.

intensity of magnetization in the plate and not to the magnetic field. The observed effect, therefore, reaches a maximum value when the intensity of magnetization has reached its greatest value.

In Table II. are recorded the Leduc coefficients $_hT_h$ for a number of metals studied together with the field strength and the temperature at which the observations were made. The sign prefixed to the coefficient indicates the direction of the effect according to the convention explained earlier in this paper. The values for iron, zinc and antimony are in good agreement with the corresponding values given by Zahn[1] but the values for nickel and cobalt do not agree well with his values. For the sake of comparison Zahn's values have been inserted in brackets. For a field of 6,290 gauss Zahn gives for another specimen of nickel the value, -55×10^8. For iron Hall and Campbell found $_hT_h = +632 \times 10^9$ at 60° C. The lack of agreement between these observed values of $_hT_h$ must be attributed for the most part to the impurities in the metals and to their previous treatment.

TABLE II.

Metal.	H	$_hT_h \times 10^8$	Temp. ° C.
Nickel	10,880	− 61.5(20)	61.0°
Cobalt	11,800	+ 64.0(13)	53.7°
Nichrome	10,800	+ 38.8	59.3°
Electrolytic iron	11,900	+ 39.2(39)	56.9°
Molybdenum	12,300	− 17.5	57.5°
Tungsten	12,200	+ 15	58.6°
Cadmium	12,200	+ 11	60.5°
Zinc	10,900	+ 12.4(12.9)	58.5°
Antimony	11.000	+262.0(200)	56.7°

The Leduc effect in two series of alloys—bismuth-antimony and antimony-zinc—has been studied. In the bismuth-antimony series of alloys the dependence of the effect on the intensity of the magnetic field was investigated for each of the plates. The results of these observations have been represented in Fig. 4. In this figure the transverse difference of temperature for a plate one centimeter wide with a temperature gradient of one degree Centigrade per centimeter has been plotted as ordinates and the magnetic field in gausses as abscissæ. It is seen from this figure that the transverse difference of temperature in bismuth and the alloys which contain a large percentage of bismuth increases less rapidly than the magnetic field. On the other hand in antimony and the alloys which contain a large percentage of antimony there is a linear

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[1] Ann. der Phys., 14, p. 886 (1904).

relation between the magnetic field and the transverse difference of temperature. The sign of the effect in antimony is opposite to that in bismuth. To show the dependence of the Leduc coefficient on the composition of the alloy Fig. 5 has been plotted with the Leduc coefficients as ordinates and the percentages by weight of antimony as abscissæ. The Leduc coefficients plotted in Fig. 5 were determined at a temperature of about 52° C. and with a magnetic field of about 11,000 C.G.S. units. The addition of antimony to the bismuth decreases the Leduc coefficient. When the alloy contains somewhat less than 70 per cent. of antimony the direction of the effect is reversed and for alloys containing more than this amount of antimony the direction of the effect is positive. The data from which this curve was plotted have been given in Table III.

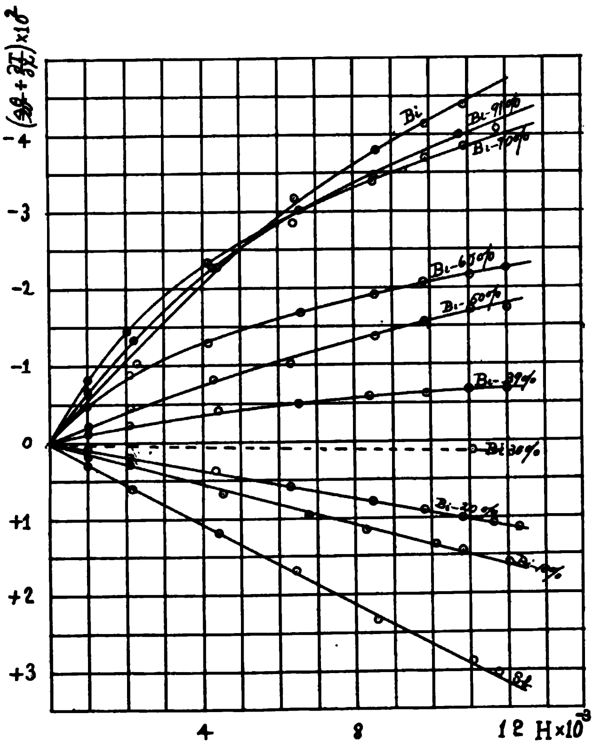

Fig. 4.

In the antimony-zinc series the Leduc coefficient for each alloy was determined only for one intensity of the magnetic field which was in the neighborhood of 11,000 C.G.S. units. The temperature on the isothermal midway between the ends of the plate was about 57° C. This is, therefore, the temperature at which the coefficients were determined. Table

TABLE III.

Composition.		${}_hT_h \times 10^8$	H
Per Cent. Sb.	Per Cent. Bi.		
0	100	−405	10,900
9	91	−375	10,800
30	70	−354	11,000
40	60	−195	11,000
50	50	−154	11,000
61	39	− 60	12,000
70	30	+ 9.5	11,100
80	20	+ 95	10,800
90	10	+132	12,060
100	0	+262	11,000

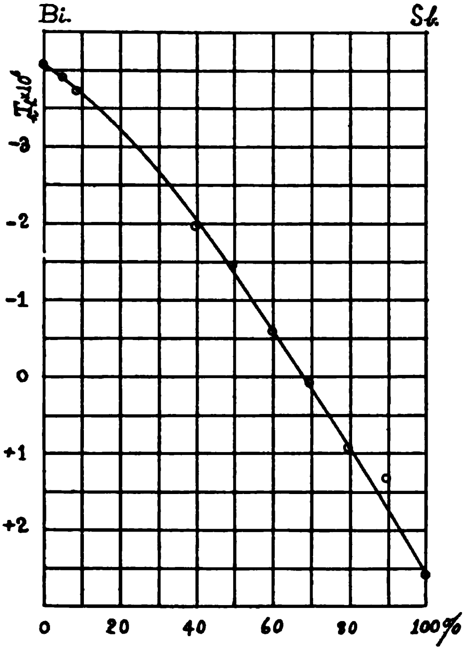

Fig. 5.

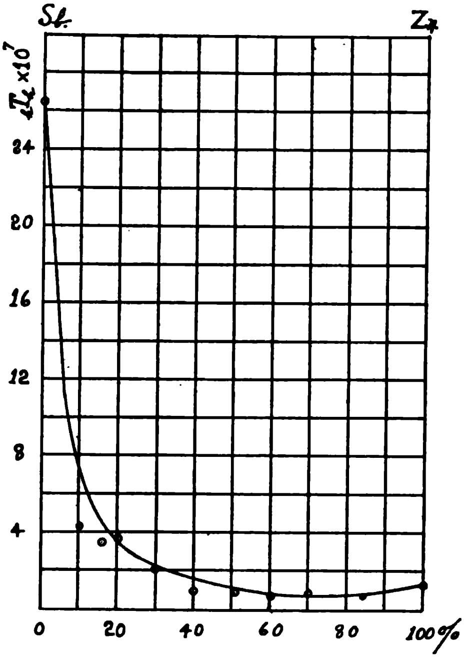

Fig. 6.

IV. gives the data on this series of alloys. These data have also been plotted in Fig. 6. The ordinates are the Leduc coefficients and the abscissæ the percentages by weight of zinc. The addition of a small percentage of zinc causes a very rapid decrease in the Leduc effect, so that when the alloy contains about 20 per cent. of zinc the Leduc coefficient is slightly more than one tenth as large as that in pure antimony. With the further addition of zinc the coefficient seems to pass through a not very well defined minimum.

TABLE IV.

Composition.		${}_hT_h$	H	Temp. °C.
Per Cent. Sb.	Per Cent. Zn.			
100	0	+262	11,000	56.7°
90	10	42.7	10,900	56.5°
84	16	32.0	10,900	57.2°
80	20	27.5	10,900	57.1°
70	30	20.9	10,900	57.5°
60	40	9.08	10,900	57.2°
50	50	8.50	10,900	55.7°
40	60	6.77	10,900	57.2°
30	70	8.40	10,900	55.3°
16	84	6.60	10,900	61.8°
0	100	12.4	10,900	58.5°

SUMMARY.

1. In the magnetic metals nickel, nichrome, iron and cobalt, the transverse difference of temperature set up by the magnetic action in the case of the Leduc effect is proportional to the intensity of magnetization in the plate and not to the intensity of the magnetic field. This difference of temperature, therefore, reaches its maximum value when the intensity of magnetization has become a maximum. The relation of this effect to the magnetic field which produces it is the same as the relation of the Hall effect and the Nernst effect to the magnetic field. In antimony the Leduc coefficient is independent of the intensity of the magnetic field.

2. The Leduc coefficient has been determined in tungsten, molybdenum, cadmium, a series of alloys of antimony and bismuth and a series of alloys of antimony and zinc.

3. The addition of antimony to bismuth decrease the Leduc coefficient but less rapidly than is to be expected from the additive law. The addition of zinc to antimony causes a very rapid decrease in the Leduc coefficient. An alloy containing 10 per cent. of zinc and 90 per cent. of antimony has Leduc effect only about one sixth of that in pure antimony. With the further increase in the amount of zinc the coefficient decreases to a not very well defined minimum from which it rises to the value in zinc.

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PHOTO-ACTIVE CELLS WITH FLUORESCENT ELECTROLYTES.

By Geo. E. Thompson.

Introduction.

The efforts of previous experimenters to prove a dependence of the photo-electric current on fluorescence, in the case where two metal electrodes immersed in certain fluorescent solutions are unequally illuminated, have not led to definite results. Minchin[1] and Hodge[2] suspected such a relation but Goldmann[3] thought the relation unlikely.

The present work was begun with the idea of securing any possible additional facts which may have a bearing on this subject. Several related facts have appeared during the progress of the work and these are also included in this paper.

Outline of Experimental Work.

Preliminary experiments were performed in order to determine what materials and solvents give the largest effect and are, therefore, most suitable for further study.

Several different metals were used as electrodes.

The fluorescence of fluorescein was increased by dilution and by addition of caustic potash and the change of current on illumination sought for.

The variation of current with wave-length of exciting light was measured in several different substances and with two types of cell.

Apparatus.

Two types of cell were used; a "Pt foil cell" and a "Ag film cell." The "Pt foil cell" was a glass box 6 cm. in depth, 1 cm. from front to back, and 4 cm. wide. Two thin strips of platinum foil about .3 cm. wide, reaching nearly to the bottom of the cell and leaving enough foil outside for making the connections to galvanometer leads, were placed about .3 cm. apart. These were held against the front wall of the cell by a piece of hard rubber and a brass spring which pressed against the

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[1] Minchin, Phil. Mag., Vol. 31, pp. 207–238, 1891.

[2] Hodge, Phys. Rev., Vol. 28, p. 25, 1909.

[3] Goldmann, Ann. d. Phys., Vol. 27, p. 449, 1908.

back wall. A paraffin stopper was used to prevent evaporation. This type of cell allowed a thin film of liquid to creep in between the electrodes and the front wall of the cell. Fig. 1 shows two views of this cell.

The "Ag film cell" had the same dimensions as the "Pt foil cell." Contact was made with precipitated silver[1] electrodes by pressing a thin sheet of tin plate against each one by means of a spring clasp clothes-pin. In order for the light to reach the liquid in this type of cell it must first pass through the silver film. These electrodes transmitted from 20 to 30 per cent. of the incident light for all wave-lengths. On account of deterioration probably due to imperfect adhesion of the silver, this cell had to be reconstructed occasionally.

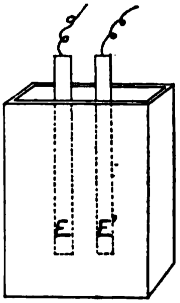

Fig. 1.

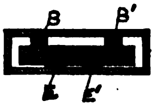

Fig. 1a.

When comparing the sensitiveness of different solutions without regard to the wave-length of the exciting light, a portion of the most active part of the spectrum from the spectrometer, described in the next paragraph, was used, or in cases where stronger illumination was required the arc light was focused upon the slit by means of a lens. A water cell was sometimes interposed to absorb heat rays but this was found to be unnecessary.

In studying the exciting power of various regions of the spectrum, a Nernst glower (110-volt A. C.) which furnished the exciting light was mounted in place of the slit of the spectrometer and an adjustable slit placed at the focus of the telescope lens permitted light of the wave-length desired to fall on one electrode of the sensitive cell. The slit width commonly used was .14 cm. The wave-length of the light used for excitation was varied by swinging the collimator arm with glower attached, the rest of the apparatus remaining fixed in position. The spectrometer arms were each about 60 cm. in length. A lead glass prism gave a visible spectrum about 7 cm. in length.

A Sullivan d'Arsonval galvanometer having a sensibility of 10^{-9}

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[1] The Rochelle salts method. See Kohlrausch's Practischen Physik, p. 36.

ampere per mm. deflection with scale at 130 cm. distance, was used for measuring the current produced by the action of the light. Ordinarily about 20,000 ohms resistance were placed in circuit to diminish the current set up by the natural E.M.F. of the cell, which could not be completely eliminated.

Method of Observation.

The light was allowed to shine on one electrode of the cell until the maximum value of current was approximately attained. This value of current was used in comparing the photo-activity of solutions. In order to obtain data for various wave-lengths of exciting light, one of the electrodes was exposed successively to the various regions of the spectrum and readings of the current taken for each setting of the spectrometer, time enough being allowed at each setting for the current to reach approximately its maximum value for that color. About thirty minutes were usually sufficient for obtaining data for a complete curve; from three to five minutes per point.

Growth and Decay of Current.

Figs. 2 and 3 show the relation between time in minutes and current when one electrode of a cell is illuminated and also the decay of the current after the light is shut off. Galvanometer deflections, which are proportional to current, have been plotted. Each figure contains curves for growth and decay of current in a strong solution of rhodamin BX in absolute alcohol with the "Pt foil cell." For obtaining Fig. 2 a strip of electrode .14 cm. wide was exposed to the light; for Fig. 3, .08 cm. in width.

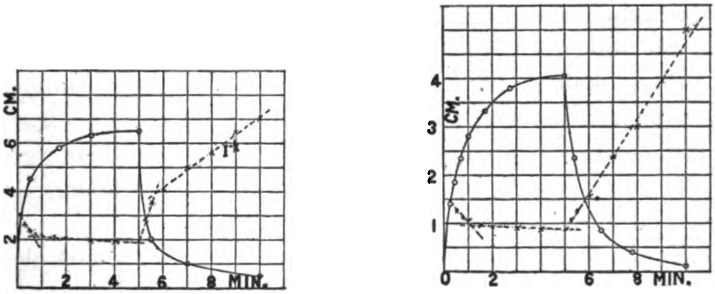

Fig. 2.

Fig. 3.

Rhodamin BX. Ordinates, galvanometer deflections in cm. Abscissæ, time in minutes.

These curves are almost identical in form with those for growth and decay of intensity of phosphorescence in many substances that possess long time phosphorescence. This similarity is made more evident by the fact that when the reciprocal of the square root of the current is plotted the broken line characteristic of phosphorescence is obtained.[1]

The same general explanation that applies to the growth and decay of phosphorescence is probably also applicable here, namely; that the total effect is the result of two effects, each of which follows a simple law, and which have different rates of growth and decay. In Fig. 3 one of these effects seems to be relatively less prominent as indicated by the more nearly linear character of the curve for $I^{-\frac{1}{2}}$.

The data obtained by Goldmann when plotted in the same way also indicate the same linear relation between $I^{-\frac{1}{2}}$ and time.

PRELIMINARY OBSERVATIONS.

In order to work with a comparatively weak source of light such as a Nernst glower where only a narrow portion of the spectrum is used it is desirable to have the most sensitive cell possible. It was found that the most fluorescent substances did not give the largest current under the action of light. Fluorescein, which was most fluorescent of all materials tried, gave a current too small to be measured when excited by the glower spectrum. Rhodamin BX, which possesses a fairly strong fluorescence, gave the largest effect of anything tried. Rhodamin R and rhodamin RRR and tetrabrom-fluorescein were mildly fluorescent and gave measurable effects. Fuchsin is weakly fluorescent but gave no current even when illuminated by the electric arc. The substances[2] tested were in all these cases in concentrated solution and used with the "Pt foil cell."

Among the solvents tried are absolute alcohol, water, grain alcohol, benzine, ether, alkaline and acidulated water and alcohol. Only alcohol dissolved sufficient quantities of the dye-stuffs for purposes of experiment so that the substances finally chosen for further experiment were rhodamin BX, rhodamin R, rhodamin RRR, tetra-brom-fluorescein and fluorescein; all in absolute alcohol.

Ordinarily the current flowed from the illuminated to the dark electrode outside the cell. The only exception noted was an alkaline water solution of fluorescein in which current could be excited only by the intense illumination of the arc. Due to the uncertainties involved in this particular case it is not quite safe to say that the current observed was a photo-electric current due to the fluorescein.

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[1] Nichols and Merritt, Phys. Rev., Vol. 27, p. 370, 1908.

[2] The rhodamin BX, tetra-brom-fluorescein, fuchsin, and fluorescein used in these experiments were obtained from Merz & Co. of New York City. The rhodamin R and RRR were kindly furnished by Prof. Orndorff of the Chemistry Department of Cornell University.

The size of the current generated by the action of light was found to be dependent upon the material of the electrodes and upon their condition. Only a few of the metals used as electrodes produced a measurable effect. Of those tried, platinum foil, silver, gold, and oxidized copper were the only ones which gave a measurable current although the more obstinate ones were exposed to the direct illumination from the arc. Zinc, iron, polished copper, lead, tin and aluminum gave no effect. Platinum foil was best and the others followed in the order named.

Photo-electric Effect and Fluorescence.

If the photo-electric current observed is directly connected with fluorescence we should expect that any increase in the fluorescence would be accompanied by an increase in the current. A dilute solution of fluorescein is more fluorescent than a concentrated solution, but repeated trials led to the conclusion that there is a loss of sensitiveness on dilution rather than an increase.[1]

The fluorescence of a fluorescein solution may be increased very markedly by adding a trace of caustic potash. Observation showed no change in the current when this was done. There is a chance here for error, however, unless all of the fluorescein is dissolved before the alkali is put in. The fluorescein is more easily dissolved after the addition of the alkali and an increase of photo-electric current which is really due to an increase of concentration may be wrongly attributed to the increase of fluorescence.

Variation with Wave-length of Exciting Light.

It has been pointed out by other observers that the maximum effect is produced in the region of maximum absorption, but definite data have not been given. Goldmann[2] found that the light included in the region of absorption produced practically the whole effect, but he did not disperse the light. Hodge,[3] and Rigollot,[4] state that the maximum effect was found on the red side of the absorption band just before entering the band. But as will be shown later this result would have been different had a correction been made for unequal energy distribution in the spectrum used for excitation.

[1] Since this work was done, a paper has been published by Mecklenberg and Valentine which states that the fluorescence of fluorescein is proportional to concentration if the absorption of the excited fluorescent light is corrected for. The above experiment is, therefore, based on a false but common assumption (Phys. Zeit., Vol. 15, p. 267).

[2] Goldmann, l. c., p. 476.

[3] Hodge, l. c.

[4] Rigollot, Journ. d. Phys. (3), Vol. 6, p. 520, 1897.

Fig. 4, Curve I., shows the variation of current with wave-length of exciting light, using the "Pt foil cell" with a fairly concentrated absolute alcohol solution of rhodamin BX; width of electrode illuminated, .08 cm. The ordinates of Curve *A* are proportional to the coefficients of absorption in a dilute alcohol solution. The general shape of the Curve *A* is the same as for a concentrated solution.[1] The fluorescence band for a dilute solution is represented approximately by Curve *F*.

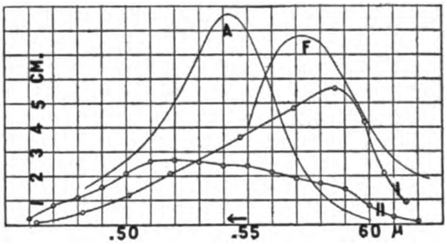

Fig. 4.

Rhodamin BX; "Pt foil cell." Ordinates of curve *A* are proportional to coefficients of absorption. Curve *F*, fluorescence; I., observed photo-electric current; II., corrected curve.

Fig. 5 shows results obtained under similar conditions except that the width of slit was .14 cm. On account of the larger current obtained, this curve is probably the most accurate of any that will be shown.

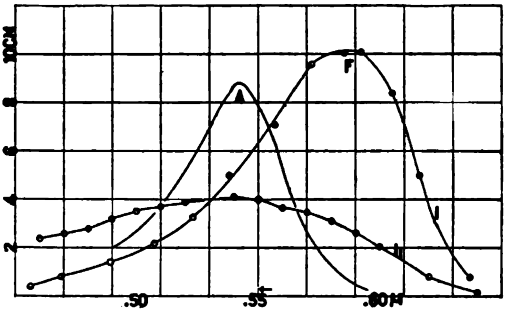

Fig. 5.

Rhodamin BX. *A*; absorption; I., photo-electric current; II., corrected curve. "Pt foil cell."

The results of Fig. 6 were obtained with the "Ag film cell" under similar conditions.

Fig. 7 contains curves for tetra-brom-fluorescein with the "Pt foil cell"; slit width, .14 cm.; absolute alcohol solution.

Fig. 8 shows two curves for rhodamin RRR using the "Pt foil cell";

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[1] Nichols and Merritt, PHYS. REV., Vol. 31, p. 376, 1910.

absolute alcohol solution. They were both obtained with the same solution but with different areas of the electrodes exposed in each case; .08 cm. for the lower curve and .14 cm. for the upper.

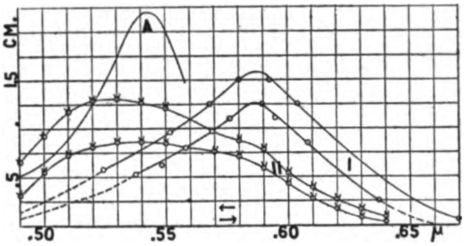

Fig. 6.

Rhodamin BX. Cell No. 2. I., observed curve; II., corrected curve. "Ag film cell."

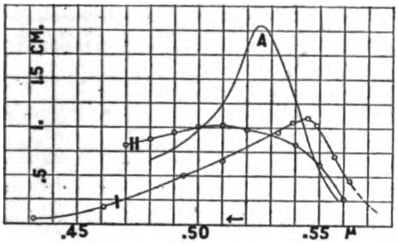

Fig. 7.

Tetra-brom-fluorescein. "Pt foil cell."

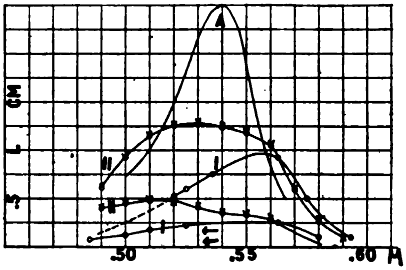

Fig. 8.

Rhodamin RRR. "Pt foil cell."

CORRECTIONS TO BE MADE.

The manner in which the photo-electric current depends upon the wave-length of the exciting light is more clearly brought out by correcting for unequal dispersion and unequal energy distribution throughout the spectrum of the glower. The dispersion for a particular wave-length was taken as an arbitrary unit with which the dispersion in other parts of the spectrum could be compared. Then for any wave-length the ratio of the dispersion to this arbitrary unit becomes the correction factor by which each corresponding ordinate of the observed curve must be multiplied in order to correct for unequal dispersion. Column 3 of Table I. gives values of these factors for various wave-lengths.

The intensity of the spectrum from the glower was then compared, wave-length by wave-length, with that of an acetylene flame by means of a spectro-photometer. Six sets of readings were taken throughout the spectrum and the average values used in computing the ordinates of the energy curve of the glower. Column 2 of the table gives the results of this comparison. The curve given by Coblentz[1] for the energy distribution of the acetylene flame afforded a basis for the computation of energy distribution of the glower from the spectro-photometric comparison. The ordinates of the acetylene energy curve were multiplied by the numbers in column 2 in order to get the energy curve of the glower. The energy of some particular wave-length was taken as the arbitrary unit and correction factors for other wave-lengths found by comparing the ordinates of the glower curve. For example, the correction factor for the wave-length whose energy is one half the arbitrary unit is 2. Column 4 contains these correction factors.

TABLE I.

DATA FOR FIG. 4.

1	2	3	4	5	6	7
Wave-length.	Ratio of Glower to Acetylene.	Correction Factors for Dispersion.	Correction Factors for Energy Distribution.	Product.	Ordinates of Observed Curve.	Ordinates of Corrected Curve.
.450		1.05	5.08	5.34	0.00	0.00
.460		.92	4.40	4.04	.07	.28
.470	.89	.90	3.66	3.29	.25	.80
.480	.94	.80	3.14	2.51	.45	1.13
.490	.89	.75	2.85	2.14	.75	1.60
.500	.89	.75	2.54	1.85	1.15	2.12
.510	.91	.71	2.20	1.56	1.65	2.57
.520	.95	.70	1.78	1.25	2.20	2.75
.530	1.00	.64	1.53	.98	2.70	2.64
.540	1.04	.60	1.32	.79	3.20	2.53
.550	1.07	.55	1.16	.64	3.80	2.43
.560	1.04	.46	1.06	.49	4.30	2.16
.570	1.01	.38	1.00	.38	4.90	1.87
.580	1.01	.35	.91	.32	5.40	1.73
.590	1.02	.33	.82	.27	5.50	1.48
.600	1.04	.32	.74	.24	3.50	.84
.610	1.08	.30	.66	.20	1.50	.30
.620	1.13	.30	.57	.17	.50	.08
.630	1.17	.30	.51	.15	.10	.02
.640	1.20	.30	.46	.14	.00	.00

The product of the factors in columns 3 and 4 (column 5) gives the number by which each ordinate of Curve I. must be multiplied. The resulting curve represents, therefore, the current which would be produced by a normal spectrum of uniform energy distribution. Column 6 gives the ordinates of the observed curve and 7 those of the corrected curve of Fig. 4.

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[1] W. W. Coblentz, Bull. Bur. of Stds., Vol. 7, p. 259, 1910.

Sources of Error.

It has been recognized that the use of the galvanometer as a measuring instrument permits the polarization of the cell and may influence the results. But since Goldmann[1] has shown that the effect is only slightly diminished by polarization and not changed in character, it seems that results obtained in this way are not invalidated. Attempts were made to avoid this by using an electrometer but a quadrant electrometer (.001 volt sensibility) did not prove sensitive enough to measure the E.M.F. developed by the glower spectrum.

The spectrum had some overlapping of colors on account of the width of the source (about .5 mm.) and all colors were not accurately focused. The focus was accurate in the yellowish green. This impurity of the spectrum would not lead to any serious error.

The fluctuations of voltage on the glower were sometimes considerable but caused no serious disturbance because of the lag of the photo-electric current behind changes in intensity of the exciting light (see Fig. 2). The tendency is, therefore, for the effect to assume a value which corresponds to the average illumination.

The sensitiveness of the cell diminished slightly with each succeeding illumination but recovered somewhat when let stand in the dark. Finally the solution had to be renewed on account of permanent loss of sensitiveness.

It was more difficult to secure data with the "Ag film cell" on account of disturbances due to slight jarring, etc. The two curves shown were the best ones observed. These show an extrapolation in the blue, but several independent observations in this region prove this to be the correct form for the curves. On account of the disturbances, observations had to be made more hurriedly with this cell; hence, the necessity for extrapolation. When the observations were made it was not realized that this was to be the important part of the curve or the extrapolation could have been avoided in this region.

The displacement of the current maximum from the absorption band toward the blue may be due in part to the fact that in those cases the observations were begun in the red. If sufficient time were not given for the current to diminish to its normal value for each color, the values to the left of the maximum on the observed curve would be too large and might shift the maximum of the corrected curve. Sufficient data is not at hand to make this conclusion certain. There is also considerable difficulty in reproducing results.

The arrows at the bottom of the figures indicate the manner in which

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[1] Goldmann, l. c., p. 500.

the readings were made; *e. g.*, an arrow pointing toward the blue means that readings were begun in the red and progressed toward the blue.

With the "Pt foil cell" we might expect the maximum to be somewhat diminished by the absorption of the layer through which the light must pass before it strikes the electrode. There is no very noticeable difference, however, between the corrected curves for the two types of cell.

SUMMARY OF RESULTS.

The curves for the growth and decay of the photo-electric current are similar to those for the growth and decay of phosphorescence. If $I^{-\frac{1}{2}}$ be plotted, the characteristic broken line is obtained.

The magnitude of the photo-electric current depends on the metal used as electrodes. Of ten metals tried, only platinum, gold, silver and oxidized copper gave a measurable effect.

The position of the maximum effect does not depend upon the material of the electrodes but upon the material in solution.[1] The effect is not the photo-electric effect of the metal in the liquid.

The experimental results do not show any close connection between the photo-electric current and fluorescence. Two methods of increasing fluorescence did not increase the current. The region of excitation for the current extends further into the red than for fluorescence.

All of the curves show the maximum photo-electric current approximately in the region of maximum absorption.

CORNELL UNIVERSITY,
July, 1914.

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[1] Rigollot has mentioned this. Journ. d. Phys. (3), Vol. 6, p. 520, 1897.

A COMPARATIVE STUDY OF THE LIGHT-SENSIBILITY OF SELENIUM AND STIBNITE AT 20° C. AND − 190° C.

By D. S. Elliott.

IT is a well-known fact that selenium experiences a decrease of resistance when exposed to light under the proper conditions, and several explanations for this fact have been offered. It was suggested by Pfund[1] that the conduction in selenium is electronic and that the increased conductivity may be accounted for on the assumption that the absorbed light sets electrons in resonance resulting in their expulsion outside the atoms. This would increase the number of electrons available for carrying the current and hence increase the conductivity.

Among the facts that can be marshalled in support of the electronic hypothesis, the most important are these:

1. As shown by Thomson in his "Conduction of Electricity Through Gases," the current through an ionized gas is proportional to the square root of the energy of the ionizing agent, provided the ionization has reached a steady state. The same law has been shown by Pfund[2] and Nicholson[3] to hold for selenium for unlimited exposures to radiation from $\lambda = 230\mu\mu$ to $\lambda = 900\mu\mu$ and for X-rays.

2. Another general property of electronic conduction is the absence of polarization. A number of investigators[4] have definitely established the fact that normal selenium cells show no polarization. This proves that the conduction is not electrolytic.

3. The retention of light-sensibility at the temperature of liquid air is also evidence for the electronic hypothesis. This property of selenium is clearly shown by the experiments of Pochettino,[5] Miss McDowell[6] and the author.

4. All light-sensitive substances show the "voltage effects"; *i. e.*, Ohm's law is not obeyed. Ries,[7] Adams[8] and Luterbacher[9] have shown

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[1] Pfund, Phys. Rev., 28, 1909, p. 324.

[2] Pfund, Phys. Rev., XXXIV., No. 5, May, 1912.

[3] Nicholson, Phys. Rev., Vol. III., Jan., 1914.

[4] Ries, "Electrical Properties of Selenium," p. 53. Pfund, Phys. Zeit., 10, 340, 1909.

[5] Pochettino, Rend. R. Accad. dei Linc., Sec. 5, Vol. II., p. 286.

[6] McDowell, Phys. Rev., 31, p. 524, 1910.

[7] Ries, Phys. Zeit., 12, p. 480 and 552, 1911.

[8] Adams, Proc. Roy. Soc., 23, 1875.

[9] Luterbacher, Ann. d. Phys., 33, 1392, 1910.

that the specific resistance of selenium decreases with an increase of voltage, and also decreases as the current continues to pass through the cell.

Object of Investigation.—As the information on selenium at liquid air temperature was not as complete as might be desired, it seemed advisable to investigate this further. The particular object of the investigation, however, was to examine other light-sensitive substances and determine whether or not they showed behavior similar to selenium at 20° C. and – 190° C. Most of the observations have been confined to stibnite.

Cells.—In order to carry out this investigation, it was first necessary to prepare cells which would meet the extreme demands necessitated by this temperature variation. It soon became evident that selenium cells prepared in the usual way would not suffice, as it was found that after a cell had been subjected to the temperature of liquid air and was brought back to 20° C., its behavior was markedly different. After some experimenting, cells were constructed according to the following design which is due to Professor Pfund. This cell has proven so satisfactory that it seems well to describe it in some detail.

Selenium Cells.—Amorphous selenium was first cast into discs about 1.5 cm. in diameter and 1.5 mm. thick. They were sensitized in the usual way, being maintained at a temperature of 200° C. for six hours and then cooled rapidly to room temperature. The discs were then ground smooth on crocus cloth, after which silver tape electrodes were fastened on with celluloid. A film of gold was next deposited by cathode sputtering, and finally the gold was removed along a narrow line like a grid as shown in Fig. 1. Attention is called to the four shallow pools of celluloid shown. Besides strengthening the construction these provide a smooth transition from the selenium to the upper surface of the silver tape. In this way fractures of the gold film were avoided. The time required for the deposition from the insertion of the cell to its removal did not exceed twenty minutes; but as a matter of fact, the selenium was covered with a protective layer of gold within six minutes. No

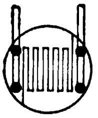

Fig. 1.

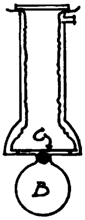

Fig. 2.

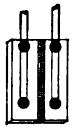

Fig. 3.

deleterious action due to mercury vapor could be detected. The cell was finally enclosed in a glass tube similar in design to Fig. 2. Bulb *B* was filled with calcium chloride and the constriction leading to the upper chamber loosely plugged with cotton. The cell "*c*" was fastened with sealing wax in this upper chamber, the end of which was closed by a glass plate. The vessel was also provided with a side tube for exhausting by means of an aspirator, a phosphorus pentoxide tube being inserted between cell and aspirator during the process.

Stibnite Cells.—Stibnite cells were made and mounted in essentially the same way as the selenium cells. Starting out with crystals of stibnite[1] (Sb_2S_3) and using the cleavage surfaces, in some cases gold was deposited over the whole surface and afterwards removed along a line by scratching; in other cases a protective layer of tin-foil about 0.5 mm. wide was placed along the middle of the surface before deposition. This tin foil was afterwards removed disclosing a strip of clean cleavage surface which could be exposed to the light. Fig. 3 is a picture of a stibnite cell.

Apparatus.—The arrangement of apparatus is shown in Fig. 4. The source of illumination was a Nernst lamp *L*; a spectrometer of the Wadsworth type broke up the radiation into quasi-monochromatic light focused in the plane of slit S_2; the light could then follow one of two paths depending upon whether the right-angle prism *P*, hinged at *H*, was raised or lowered. With the prism *P* swung out of the way, the light was focused by the lens L_2 on a sensitive thermal junction. This system, constructed according to his latest design,[2] together with a sensitive galvanometer, was built by Professor Pfund and kindly placed at my disposal. Its sensibility was such that a candle at a meter's distance gave a deflection of 30 mm. With the prism *P* down, the light was diverted downward upon cell "*c*" which was inserted in a Dewar flask. The amount of glass in the path of the beam over both paths was approximately the same, and it might be said at this point that in carrying out any set of experiments to determine the effect of temperature or anything

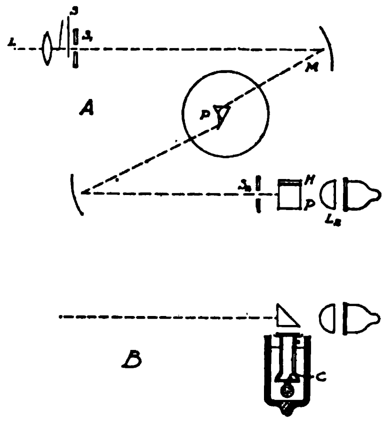

Fig. 4.

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[1] The crystals of stibnite were generously furnished by Dr. W. W. Coblentz of the Bureau of Standards.

[2] Pfund, Phys. Zeit., XIII., 870, 1912.

else, that particular factor could be varied alone without disturbing the cell in any way. Results obtained are therefore strictly comparable.

In measuring increased conductivity the usual method was employed. Diagram 5 shows the arrangement. In some cases a counter E.M.F. was introduced at the galvanometer terminals to annul the "dark deflection," and when the increased conductivity was too large, a shunt R was introduced to cut down this deflection. In some cases both the counter E.M.F. and the shunt were unnecessary. Both this galvanometer (sensibility 1.5×10^{-8} amperes) and a device for exposing for the desired time, were placed in an adjoining room. In general, exposures of ten seconds were taken, and an interval of three or four minutes elapsed between readings.

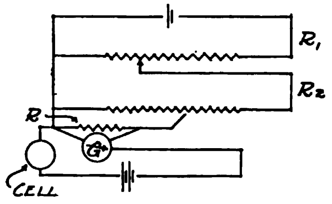

Fig. 5.

Sensibility Curve. Selenium 20° C.—In these observations, cells of the new design were used. Strictly speaking the sensibility of a cell is the ratio of the two quantities—the change in resistance per unit energy illumination, and the dark resistance. The quantity used in plotting these curves is proportional to this. The galvanometer deflection corresponding to a certain value of incident energy was first obtained. The deflection corresponding to a particular value of energy taken as unity could then be calculated from the relation $D = KE^{\beta}$ where D is the galvanometer deflection, K a constant, E the incident energy and β another constant. For unlimited exposures, Pfund and Nicholson have shown that $\beta = 0.5$, and this is the value used in applying the formula unless definitely stated otherwise. Attention is called to the fact that actual observations near the sensibility maximum were taken for energies which do not vary appreciably from the value of energy taken as standard. This was accomplished by adjusting the voltage on the Nernst lamp and the width of the slit S_1. In this way all possibility of vitiation of the results by the assumption of any law connecting galvanometer deflections and energy was obviated. Curve I. gives the sensibility curve for selenium cell D, temperature 23°.5 C., 120 volts.

Sensibility Curves of Selenium at − 190° C.—In taking these curves the Dewar flask was filled with liquid air and replaced about the cell. This adjustment could be effected without disturbing the rest of the apparatus. Sufficient care was taken to see that the flask remained well filled with liquid air. By means of a funnel arrangement, not shown in the drawing, the supply of liquid air could be replenished without withdrawing the flask, so that the cell remained undisturbed in liquid air throughout the experiment. In all recorded experiments the cell was brought to this low temperature very gradually, and throughout the procedure the conductivity was observed to fall very rapidly until it

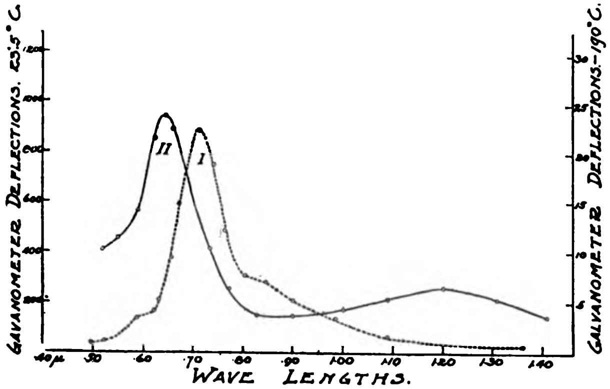

Fig. 6.

became barely perceptible. Observations of Pochettino[1] and Miss McDowell[2] also show that the resistance of selenium at liquid air temperature is enormously great.

In the early part of the work some experiments were carried out to determine whether or not the ratio of the increased conductivity to the original conductivity—$\Delta c/c$—was independent of the temperature for any one wave-length. Fig. 7 gives the arrangement of the apparatus for this part of the work. The circuit containing the cell c and a storage battery B was completed through S the secondary of a transformer; the primary coil P was connected to a sensitive galvanometer G. Exposures of 0.2 second were obtained by means of a pendulum also shown in the drawing, and a device was fixed to the pendulum so as to break the primary circuit slightly before the exposure of 0.2 second was completed. In some cases $\Delta c/c$ was independent of the temperature, in other cases this ratio increased with temperature, while in still other cases it decreased as the temperature was raised. In all cases, however, the results were of the same order of magnitude. A possible explanation based on a change of optical properties is suggested from a consideration of the change in sensibility curves for the two temperatures. The striking fact, however, is that the light becomes

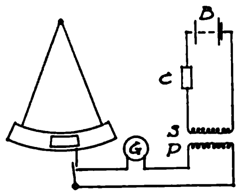

Fig. 7.

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[1] Pochettino, Rend. R. Accad. dei Linc., Sec. 5, Vol. II., p. 286.

[2] McDowell, Phys. Rev., 31, p. 524, 1910.

effective at the temperature of liquid air just as rapidly as at ordinary temperatures, while the recovery for the lower temperature is very much slower.

A typical sensibility curve for selenium at – 190° C. for a ten-second exposure is shown in Curve II. In making all observations at liquid air temperature, the cell was afterwards brought back to room temperature to determine whether or not the first readings could be reproduced. This is the reason why early observations on cells of standard design were discarded as worthless. With the new design no difficulty was experienced.

Voltage effects were detected at liquid air temperature.

From a comparison of Curve I. and II. the following conclusions seem to stand out most pronounced: Lowering the temperature of selenium from 20° C. to – 190° C. causes

1. An extension of the range of sensibility from 0.9 μ to 2.0 μ approximately.
2. A shift of the sensibility maximum towards the region of shorter wave-lengths by about 600 A.U.

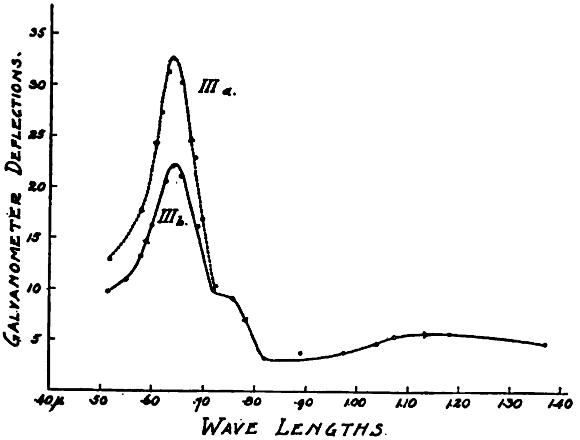

Fig. 8.

The position of the sensibility maximum is unaffected by the voltage effect and the direction of progression through the spectrum. This is shown by Curves III_a and III_b which refer to selenium at – 190° C. Curve III_b as indicated by the arrow is plotted from readings taken through the spectrum from shorter to longer wave-lengths, Curve III_a refers to the same cell, readings being taken in the reverse order. During the course of the readings the conductivity was observed to increase appreciably although the temperature must have remained constant. The position of the sensibility maximum, however, is unaffected.

Stibnite.—The light sensitive property of stibnite (Sb_2S_3) was discovered by Jaeger[1] in 1907, and Ries[2] showed later that this substance exhibits the same voltage effects as selenium. It was decided to investigate this substance further, using as the mode of attack the sensibility curves obtained under various conditions. The cells were mounted in the same way as the selenium cells previously described.

Law Connecting Energy and Deflection. Room Temperature.—In investigating this point a rotating sector was placed before the spectrometer slit S_1 (see Fig. 4). The disc was so constructed that by sliding the motor along a pair of ways, full, one half, or a quarter energy was allowed to fall on the slit, and the resulting galvanometer deflections could be obtained. The accompanying table is representative of this part of the work.

Exposure 10 sec. 110 volts. 21° C.

Wave-lengths.	D_1=Galv. Defl. Full Energy, Mm.	D_2=Galv. Defl. ½ Energy, Mm.	D_3=Galv. Defl. ¼ Energy, Mm.	β Calc. from D_1 and D_2.	β Calc. from D_1 and D_3.
0.642μ	9	6.2	4	0.54	0.58
.670	16	11	7.7	0.54	0.53
.685	27.5	19.3	13.7	0.51	0.53
.700	59	39	26.7	0.59	0.57
.740	137.5	95.1	66.7	0.53	0.52
.768	86.75	54.5	35.8	0.67	0.64
.800	39.5	23	15.1	0.78	0.69
.873	7	3	2	1.02	0.92

Exposures of ten seconds were made, and the relation $D = KE^\beta$ was assumed to hold between galvanometer deflection D and the energy E. Having two values of D as well as the ratio of the corresponding energies, the value of β is easily calculated. It will be observed from the foregoing table that the value of β for shorter wave-lengths is in general less than for the longer wave-lengths. This is similar to what we find in selenium. The obvious explanation is that a greater time is required for equilibrium for the longer wave-lengths. For the same reason the value of β for all wave-lengths is too large. For exposures sufficiently long enough to ensure equilibrium, it is safe to say that the square root law holds for stibnite. In other words, stibnite obeys the law $D = KE^\beta$ where D is the galvanometer deflection, K is a constant, E the energy and $\beta = 0.5$ approximately.

Sensibility Curve for Stibnite at Room Temperature.—Two specimen sensibility curves will be given in this connection. Both refer to the

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[1] Jaeger, Proc. Roy. Acad. Sci. Amsterdam, 9, 808, 1907.

[2] Ries, Ann. d. Phys., 36, 1911, p. 1055.

same stibnite cell—cell "*A*," which had a scratched surface. The first observations were taken by exposing the cell until equilibrium was reached. Owing to the voltage effect in stibnite the galvanometer never came absolutely to rest, but equilibrium was considered to have been reached when the galvanometer moved less than 1 mm. per minute. After each reading the cell was allowed to "soak" back approximately to its original conductivity before the next reading was taken. Intervals between readings amounted in some cases to as much as thirty-five minutes. Curve IV. gives these results. Curve V. refers to the same cell, readings being taken for exposures of ten seconds. All other conditions were practically the same. Comparing Curves IV. and V., we see that for unlimited exposures the sensibility maximum lies further in the red. An explanation of this fact is that while equilibrium is approximately reached for the shorter wave-lengths in ten seconds, such is not the case for the other end of the spectrum. The effect of longer exposures is therefore to increase the ordinates corresponding to longer wave-lengths, leaving the short wave-lengths practically unaffected. Consequently the maximum shifts towards the longer wave-lengths.

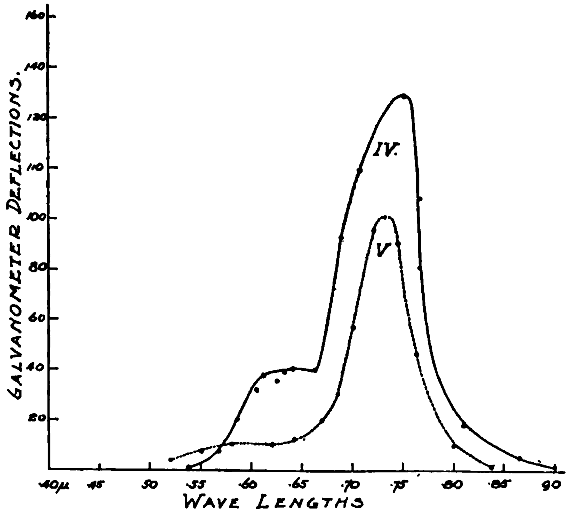

Fig. 9.

Voltage Effects.—As other investigators[1] have already observed, stibnite shows the voltage effects. The specific resistance decreases with the voltage; and for the same voltage, the resistance decreases with time. Like selenium, stibnite cells do not regain their original conductivity

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[1] Ries, Ann. d. Phys., 36, 1655, 1911.

immediately but require time. Compared with selenium, however, this return is much more rapid.

Stibnite at the Temperature of Liquid Air.—Sensibility curves were obtained at this temperature, and the law connecting galvanometer deflections and energy investigated. A cursory examination seemed to indicate that at this temperature the square root law held for equilibrium exposures, but as it was proposed to use an exposure of ten seconds for the sensibility curves, the law connecting energy and deflections was investigated under these conditions. The data referring to this part of the work follows:

Stibnite Cell "*D.*" Temperature – 190° C.
Voltage 120. Exposure 10 sec.

Wave-lengths.	D_1 = Galv. Defl. Full Energy. Mm.	D_2 = Galv. Defl. Half Energy, Mm.	β Calc. from D_1 and D_2.
0.577	13.65	8.3	0.71
0.616	17.25	10.14	0.74
0.735	21.6	12	0.85
0.813	30.9	17.97	0.78
		Mean value	0.77

Sensibility Curves of Stibnite at – 190° C.—A number of experiments were carried out on different cells of both the scratched and the unscratched variety. Curve VIII. is a typical curve. Although the value

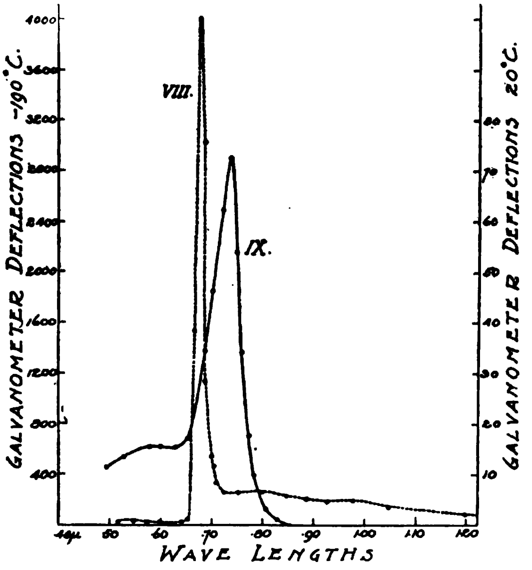

Fig. 10.

of β used in reducing the deflections to equal energies was 0.77, a calculation showed that there would be no sift of the position of the sensibility maximum for values of β ranging from 0.5 to 1.0. Curve IX. refers to the same cell at room temperature.

From a comparison of Curves VIII. and IX., these two conclusions stand out most prominently: Lowering the temperature of stibnite from 20° C. to − 190° C. causes:

1. Extension of the region of sensibility to 2 μ approximately.
2. Shift of the sensibility maximum towards the region of shorter wave-lengths by about 600 A.U.—approximately the same as for selenium.

Anomalous Stibnite Cells.—In addition to the general characteristics enumerated above, two cells—stibnite cell "*B*" and stibnite cell "*X*," exhibited some surprising properties. A preliminary test with an incandescent lamp indicated that these cells were quite normal, but with monochromatic light some unexpected properties were found. For certain regions of the spectrum these cells were photo-negative, while for longer wave-lengths they were photo-positive. The performance of stibnite cell "*B*" is given in the following table:

Stibnite Cell "*B*." Temperature 20°.5 C.
Voltage 20. Exposure 10 secs.

Wave-lengths.	E_1 = Energy Defl., Mm.	D_1 = Galv. Defl., Mm.	E_2 = Energy Defl., Mm.	D_2 = Galv. Defl., Mm.
0.5035μ	11.5	− 8	2.0	− 5
0.5302	20.5	−10	3.25	− 5
0.5602	40	− 7.5	7	− 7
0.5936	79	−10	14.5	− 7.4
0.634	160.5	− 5.2	31	− 5
0.657	219	0	47.5	0
0.695	229	+16	54	+ 9
0.724	234	+18	57.5	+10.5
0.767	198	+19.5	54.5	+ 4
0.806	185			

It seems well to mention that whenever the deflection was negative, an additional negative deflection was observed immediately after the light was turned off. Just what the explanation is, it is impossible to say, but it is certain that the effect is in the cell itself and is not due to external electrical influences. Glancing at the table, it is seen that no deflection is recorded for $\lambda = 0.657\ \mu$. The inference must not be drawn from this that the galvanometer remained entirely quiescent. As a matter of fact there was first a positive deflection of 1.5 mm., followed immediately by an equal negative deflection. No simple relation was found connecting energy and deflection. It is evident that we are dealing here with the superposition of two effects. A superficial study shows that if the law $D = KE^{\beta}$ does apply, the values of β for the positive and the negative effects are entirely different.

At the temperature of liquid air this cell showed the maximum in the usual position. At this temperature the negative effect was entirely absent; the range of sensibility had been extended considerably, positive deflections being recorded from 0.48 μ to 2.5 μ. Returning to 20° C. the cell was found to be light negative again. The writer hopes to investigate photo-negative selenium cells prepared according to Brown's process,[1] to see whether or not this photo-negative property is fundamental in character.

Stibnite cell "*X*" when first prepared showed this photo-negative property even more strikingly than cell "*B*." Twenty-four hours later this had entirely disappeared and the cell though unsteady was normal in its behavior. The transient character of this photo-negative property as indicated by cell "*X*" is controverted by cell "*B*" fully described above. At the time of writing cell "*B*" which is a month old still retains its photo-negative characteristics. Further studies of these so-called anomalous cells are to be made with a more rapidly moving galvanometer.

Theoretical Discussion.

More extended experimental data must be at hand before a theoretical discussion becomes profitable. It will be remembered however that Pfund[2] found the sensibility maximum of selenium to lie in the region of increasing transparency. Nicholson's[3] experiments also have a bearing in this connection. Koenigsberger[4] and Mueller[5] have found for stibnite an increasing transparency at the edge of the visible spectrum and Trowbridge[6] found a temperature shift of the transparency maximum of molybdenite of about the same magnitude as was found in these experiments for the sensibility maximum. While the evidence is far from conclusive, one is naturally led to look for some connection between the electrical and optical properties in selenium and stibnite. Bearing this in mind, it is to be remembered that only investigations of the optical and electrical properties which are carried out on the same sample, are comparable. If it should happen that a parallelism exists between the optical and electrical properties of these two substances,

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[1] Phys. Rev., Vol. 1, series II, p. 237; Phys. Rev., Vol. 1, series II, p. 245.

[2] Pfund, Phys. Rev., XXVIII., No. 5, 1909.

[3] Nicholson, Phys. Rev., Vol. III., No. 1, 1914.

[4] Koenigsberger, Ann. d. Phys., Band 43, heft 8, p. 1205, 1914.

[5] Mueller, N. J. F. Min. Blbd. 17, 244, 1903.

[6] Trowbridge, Phys. Rev., Vol. II., No. 5, Nov., 1905.

then there can be no doubt that the mechanisms of absorption and increased conductivity are intimately connected.

SUMMARY.

To summarize the results of this paper:

1. A new form of selenium cell has been prepared particularly adapted for low temperature work.

2. Sensibility curves of selenium and stibnite at 20° C. and − 190° C. show that lowering the temperature causes: (*a*) A shift of the sensibility maximum towards the region of shorter wave-lengths by about 600 A.U. for both stibnite and selenium; (*b*) An extension of range of sensibility from 0.9 μ to at least 2 μ for both selenium and stibnite.

3. Sensibility curves for the same stibnite cell for both equilibrium exposures and exposures of ten seconds show a shift towards longer wave-lengths for the equilibrium exposures.

4. Investigation of the law connecting deflections and energy shows: (*a*) For equilibrium exposures, both stibnite and selenium obey the square root law, *i. e.*, $D = KE^{\beta}$ where-$\beta = 0.5$ approximately. (*b*) For stibnite at − 190° C., exposure ten seconds, $\beta = 0.77$.

5. Both selenium and stibnite show voltage effects.

6. These results seem to indicate that the mechanism which brings about light sensitiveness in selenium and stibnite is of the same general character.

In conclusion I wish to thank Professor J. S. Ames for suggesting the problem and for his interest throughout the investigation. To Professor A. H. Pfund for his many helpful suggestions and his constant encouragement I wish to express my sincere appreciation.

JOHNS HOPKINS UNIVERSITY,
May, 1914.

AN EXTENSION TOWARD THE ULTRA-VIOLET OF THE WAVE-LENGTH-SENSIBILITY CURVES FOR CERTAIN CRYSTALS OF METALLIC SELENIUM.

By L. P. Sieg and F. C. Brown.

IN a recent paper[1] we published a number of characteristic wave-length-sensibility curves for certain crystals of metallic selenium. We were unable with the apparatus then employed to carry our curves below wave-length .50 μ with any great degree of certainty, on account of the small amount of energy available from the Nernst glower in this region. We have recently employed a right angled arc, focusing the positive crater of the arc upon the slit. By means of this intrinsically brighter source we have been able to go to the limit of Hilger's monochromatic illuminator, .38 μ. A new instrument that will enable us to work in the ultra-violet region has been ordered, and as soon as it is received we propose to explore these crystals still further into this region. On account of the delay that may be involved at this time in getting this instrument we have thought it best to publish the work as far as we have carried it.

The apparatus employed was the same as that described in our previous paper[2] with the two exceptions of the arc light mentioned above, and a new Leeds and Northrup galvanometer substituted for the Siemens and Halske Panzer galvanometer. The arc light was much less steady than the Nernst glower, but by careful adjustment and attention we were able to get results that were sufficiently reliable to represent without question the true character of the curves. The D'Arsonval galvanometer was only slightly below the Panzer galvanometer previously used in working sensibility, but was vastly more steady in its action. Its resistance, and critical damping were each about 12 ohms, its sensibility 324 megohms, or 14.5 mm. per microvolt. The period was 7.3 sec. Adjustment for equal energy was made with a thermopile in just the same manner as in our previous work. Again the question whether equal energy falling upon these brilliantly reflecting crystals means equal absorbed energy among the various wave-lengths must be held in abeyance until some of their optical properties can be determined.

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[1] Phys. Rev., 4, 1914, p. 507, 1914.

[2] Loc. cit.

The curves published in the former paper, to which this paper is an addendum, indicated in every case that the light sensibility was increasing as one proceeded below wave-length .50 μ. The indications pointed not only to an increase, but to a pretty sharp increase in sensibility. Our present work was done in the hope of locating a maximum in this region, but as far as we have gone the curves still rise, indicating the maximum, if there be any at all to be further into the ultra-violet. In the accompanying figure will be noted characteristic curves for two types of crystals, the lamellar and the acicular.[1] The former crystal was clamped between two conducting jaws and its thin edge was illuminated. The other crystal was similarly clamped, and was illuminated along its whole length a distance of about 7 mm. In both cases the action was what we called "direct," as distinguished from "transmitted" action. In other words, in this case, the light fell upon the conducting portion of the crystal. It should be noted that the energy used in these last experiments was about ten times as large as the energy employed in the work already referred to.

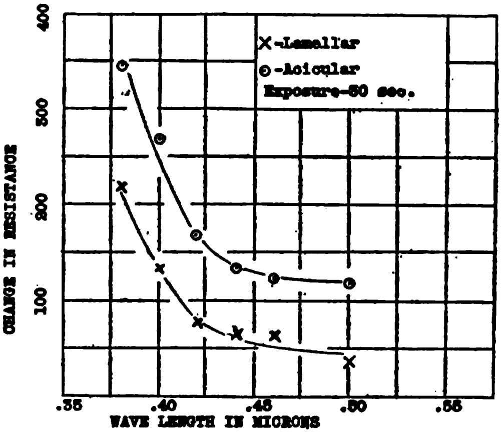

Fig. 1.

While it is unwise to make too close a comparison between the results from these crystals and those of work done on ordinary selenium cells,[2] it is interesting to note that although many of the characteristics are similar particularly with respect to light of the longer wave-lengths, there seems to be more of a difference when one deals with the shorter wave-lengths. For example we have thus far found no crystal that did

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[1] For descriptions of these crystals, and for other references, see the paper previous to this; loc. cit. Also PHYS. REV. N. S., Vol. 4, p. 85, 1914.

[2] PHYS. REV., 4, 1914, p. 48.

not indicate an increase of sensibility toward the ultra-violet, whereas many of the cells tested showed a falling off in sensibility in this region. Nicholson[1] has carried some ordinary cells down to wave-length .23 μ, and has found a steady decrease in sensibility with the shorter-wave-lengths. As we noted above, however, there is no great value in making too close comparisons, because the peculiar mat, grey surface of the common selenium cell may react toward light in a manner decidedly different from that of these brilliant crystals.

It is interesting, even at the cost of going over old ground, to speculate upon what is going on in these crystals under light action. The increase in electric action toward the ultra-violet suggests a photo-electric effect. If that is the case then it becomes difficult to account for the maximum that appears in various places toward the red end of the spectrum. In the broad sense it is of course a photo-electric effect, only in this case it is not limited to the surface but takes place throughout the body of the crystal. And it must be remembered that it takes place through the crystal not only in the path of the light, but the action spreads to a distance, as we have already shown,[2] even going from the tip of a spine down into and through the main stem of a crystal cluster. If we are dealing here with the ordinary photo-electric effect, then we should find, when we proceed into the ultra-violet, no maximum whatever, but rather a steady increase in sensibility. It may be that there is a fundamental curve for the light-electric effect on the basis of Planck's theory which will show a steady increase in proceeding from the long to the short wave-lengths, and that the various maxima found in between will find their explanation in the common optical properties of these crystals, such as selective absorption, selective transmission, body color, etc. The fact that these peculiar maxima have thus far made their appearance in the red region of the spectrum, coupled with the fact that the color transmitted through these crystals is reddish in color may be of importance in the final solution. Work along this line is to be prosecuted at once.

Physical Laboratory,
State University of Iowa.

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[1] Phys. Rev., 3, 1914, p. 1.
[2] Phil. Mag., 28, 1914, p. 497.

NOTE ON THE INDUCTION COIL SPARK.

By Will C. Baker.

It is well known that the spark of an induction coil following the "make" of the primary current is composed of a series of discharges; and similarly at "break." These are usually *assumed* to be oscillations in the secondary circuit consequent upon the single impulse due to the rise or to the fall of the current in the primary. The following observations show that, in certain coils at least, these partial sparks are not oscillatory but in each case consist of groups of unidirectional pulses.

An induction coil[1] capable of producing a 40-centimeter spark was energized from a 110-volt circuit through a variable resistance. The make and break was effected through an arm attached to a motor driven shaft, contact being made once every revolution with a fixed brush as in Feddersen's apparatus for the analysis of condenser sparks.[2] This rotating shaft carried also the metallic mirror in which the sparks were observed. The terminals of the secondary of the coil were attached to spherical brass electrodes, one of which was carried on a rack and pinion to enable the spark length to be adjusted. In order to suppress the explosions of metallic vapor studied by Battelli and Magri[3] and the "streamers" of Schuster and Hemsalech[4] the spheres were covered with cheese cloth kept wet with dilute sulphuric acid. The discharges thus took place between liquid electrodes.

Under these circumstances each partial spark shows a bright spot where it joins the cathode but none at the anode. This polarity enables one to see that the partial discharges at "make" are all in one direction and that the partial discharges at "break" are all in the opposite direction. The fact that the polarity of the discharges visibly reverses between "make" and "break" shows that there is no "valve action" in the system, for in that case one set or the other would be suppressed. This still leaves open the *possibility* that the current in the secondary may be of the nature of a small unidirectional current of relatively long duration and that as it raises the electrodes to sparking potential they

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[1] Made by Queen and Co.

[2] Wiedemann, Lehre von der Elektricität, IV, 394.

[3] Sci. Abstr., *1671* (1907).

[4] Sci. Abstr., *1066* (1900); also Milner, Sci. Abs., *269* (1909).

discharge in a spark and are loaded up again time after time by the current. To show that the effect was not this result of the capacity of the electrodes, a small Geissler tube was put in the circuit between one electrode and the coil. An examination of the phenomena at the electrodes of the tube showed that the unidirectional pulses existed in the conductor leading to the spark gap. Even after cutting out the spark gap between the spheres so that the Geissler tube short-circuited the secondary of the coil the same result was obtained. These observations seem to show that the current delivered at the terminals of the secondary coil consists of a series of pulses as described above.

There are always fewer partials at "break" than at "make" owing to the arc formed at the interrupter in the former case. For short gaps at "make," twenty to fifty partials could be seen, but as the gap widened the number diminished to one or two. The first or "pilot" spark of one of these series was usually thick and of a brilliant spark white. This was followed by a series of purple "brush-light sparks,"[1] and these again by a set of thin spark white partials that closed the series. It seems that these purple sparks are carried by the ions left by the very energetic pilot spark, and when this ionization has decayed to a limit the third group obtains. These sparks do not seem to supply ions in quantities sufficient to compensate for the decay of those produced by the first spark. Often the final set, after its first or second white spark, may include one or two purple ones, and these in every case noted show the same polarity as the second set. This idea of the cause of the change in the nature of the sparks is supported by the fact that a current of air across the gap will reduce the purple sparks almost to zero, as the ions left by the pilot spark are swept away by the blast.

These partial sparks are not due to any vibration of the brush at the interrupter, as they persist unchanged with different types of brush and with a mercury break as well. A further proof of this is found in the fact that the same phenomena occur at break, *i. e.*, after all connection with the mains, brushes, etc., has been broken. The effect may be seen with a spark gap of two metal balls, but here the "streamers" and explosions of metallic vapor referred to above render it less prominent.

The Geissler tube in no case gave indications of these three stages of the sparks which fact bears out the idea given above, as the gas in tube is more easily ionized than that in the air gap.

The same phenomena, only on a smaller scale, were observed with a coil capable only of a 15-centimeter spark.[2]

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[1] See Toepler, Ann. d. Physik, *2* (1900).

[2] From Gaertner and Co.

BEADED SPARKS.

Under certain conditions the pilot spark shows a definite structure, being a thick spark white for two thirds of the way across and for the rest of the way a purple brush. The partial sparks exhibit also variations of intensity or "beads" suggesting strongly the beaded lightning of the meteorologist. These are best developed by putting in series with the Feddersen break, an electrolytic interrupter of the Wehnelt type. The one that gave the best effect was of platinum wire 0.25 mm. in diameter, projecting 3 mm. from the protecting glass. This arrangement gives strong partial sparks due to the sharp interruption of the Wehnelt. Using liquid terminals, as above, one finds, for spark lengths of 2 or 3 millimeters a bright pilot spark followed by a series of purple sparks. On widening the gap brilliant spark white spots appear on the partials, like white beads on a purple string. Sometimes three or four on a single partial. These are not due to harmonics or to superposition as in the cases reported on by Hemsalech[1] and by Léauté,[2] for they occur irregularly both in time and in position nor are they effects of gas set free from the electrodes as in the cases referred to by Battelli and Magri[3] for they exhibit no "trajectories" in the successive partials. They appear to be due to the irregular removal of the ions left from the previous discharge, the spark showing purple in those regions where sufficient ions remain to carry the discharge, and "sparking" across those regions from which the ions have been removed by the field, or by the irregular air disturbance due to the explosion of the preceding partial. The time interval from partial to partial was estimated, from observations of displacement of the image in the mirror, at about one five thousandth of a second.

This view of the cause of the spots is borne out by the following observations: While the wind from the rotating mirror seems to have no appreciable effect (plate glass shield), an air blast across the gap causes the beads to appear in a set of sparks otherwise wholly purple, the beads being longer as the blast is stronger. Thus with a gap of 6 or 7 millimeters one can pass, altering the air blast alone, from (1) a series of purple columns (for no blast); through (2) purple columns with one or more white beads; to the case where (3) the beads lengthen, leaving the purple shrunken to a few dark spots in a brilliant white column; and finally, with stronger blast still, to (4) full bright sparks with no dark spots at all. In the cases between (2) and (3) one can often see tiny ramified brushes extending through the purple from one white bead to

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[1] Sci. Abs., *1140* (1908).

[2] Sci. Abs., *1291* (1908), and *277* (1909).

[3] Sci. Abs., *1671* (1907), and *137* (1910).

the next, just as though the beads were metal electrodes with a brush arc between them. Or when one finds a single white bead near the middle of the spark the brushes extend from the electrodes gathering in as they approach the bead from both sides.

This suggestion as to the origin of the beads receives further support from the fact that between stages (1) and (2) when only single beads are found on a few of the partials they are, *independently of the direction of the current, always opposite the smaller electrode*, where of course the field would remove the ions most rapidly. The beads were observed with the smaller coil as well. Interrupters of much larger carrying capacity than the one referred to above gave heavily mantled sparks with no beads, owing probably to the greater number of ions produced at each partial discharge. The necessary conditions for the beads seems to be a series of impulses bringing the electrodes sharply to disruptive potentials and recurring so quickly that each spark finds the partly ionized path of its predecessor.

Physical Laboratory,
School of Mining,
Queen's University,
Kingston, Ont.,
September 2, 1914.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

CHICAGO MEETING, NOVEMBER 27 AND 28, 1914.

MINUTES OF THE SEVENTY-FOURTH MEETING.

A REGULAR meeting of the Physical Society was held at Ryerson Laboratory, University of Chicago, Friday and Saturday, November 27 and 28, 1914. The Friday session was in charge of a local committee consisting of R. A. Millikan, A. A. Michelson, and Henry Crew. On Friday evening the Physical Society were the guests of the University of Chicago at the lecture of Professor W. H. Bragg of Leeds University, England.

Friday Afternoon, 2:00 P. M.

Symposium on Spectroscopic Evidence Regarding Atomic Structure. The following different aspects of the topic were presented:

The Nicholson Atom	H. B. Lemon.
The Ritz Theory	Henry Gale.
The Stark Effect	G. S. Fulcher.
Energy Relations in Light Excitation by Impact	G. W. Stewart.
X-ray Spectra	Karl Darrow.

Each topic was followed by a general discussion of about twenty minutes. Adjournment 5:45 P.M.

Friday Evening, 8:15 O'clock.

Lecture by Professor W. H. Bragg in Kent Theater on "X-ray Spectra and the Nature of X-rays." (Illustrated by slides and models.) Followed by reception at the Quadrangle Club.

Saturday Morning, 9:00 O'clock.

The Application of the Electron Theory to the Explanation of the Electrical Conduction in Crystals of Metallic Selenium. F. C. **BROWN.**

Some Fundamental Electro-mechanical and Photo-electrical Relations in Isolated Crystals of Selenium. F. C. **BROWN.**

Light-Sensibility Curves for Certain Crystals and Metallic Selenium, and their Significance. L. P. **SIEG.**

On the Reflecting Power of a Certain Selenium Crystal. L. P. **SEIG.**

Transmission of Sound Through Fabrics. F. R. **Watson.**

A Differential Dynamic Method for the Accurate Determination of the Vapor Pressure Lowering of Solutions. E. W. **Washburn.**

A Method for Determining the Variation of Frequency of the Light Emitted with the Speed of the Source. G. S. **Fulcher.**

Note on the Polarization and Absorption of Light by a Narrow Slit in a Thick Screen. G. W. **Stewart.**

The Leading Characteristics of the Electric Furnace Spectra of Vanadium and Chromium. (By title.) **Arthur S. King.**

Note on the Optical Constants of Nickel Cathode Films. L. R. **Ingersoll and** G. L. **Luke.**

Determination of the Wave-length of Characteristic Roentgen Rays by Means of Diffraction and by the Photo-electric Effect. (By title.) **Oscar Alan Randolph.**

Experiments on the Width of Spectral Lines. A. T. **Dempster.**

Thermal Radiation. **Max Mason and Otto Zobel.**

Radioactivity of Spring Water. R. R. **Ramsey.**

Saturday Afternoon, 2:00 O'clock.

Spark Discharges Between Unlike Metals. **Daniel L. Rich.**

The Arc in a Longitudinal Magnetic Field. (By title.) R. F. **Earhart.**

Thermal Capacity of Tungsten at Incandescent Temperatures, and an Apparent Lag of Radiation Intensity with Respect to Temperature. A. G. **Worthing.**

A Method for the Determination of the Law of Variation of Mass with Velocity for Cathode Rays. L. T. **Jones.**

Saturation Value of the Intensity of Magnetization of an Iron-Cobalt Alloy. E. H. **Williams.**

The Direct Current Corona of a Wire Through a Circular Opening of a Disc. L. W. **Faulkner.**

Experimental Determination of the Relation between the Corona Current and the Increase of Pressure due to D.C. Corona; Possibilities of a High Potential Voltmeter Based on this Pressure Phenomenon. (Presented by **Jakob Kunz.**) E. H. **Warner.**

Determination of the Elementary Charge of Electricity by Means of Magnetic Properties and the Magneton. **Jakob Kunz.**

A Comparison of Simultaneous Measurements of Short Distances between Conducting Flats in Air, by the Optical Electrical Method. L. E. **Dodd.**

The Law of Fall of a Droplet through Hydrogen. R. A. **Millikan and** W. H. **Barber.**

The Variation of the Wave-Length Sensibility Curves of Selenium with Temperature. E. O. **Dieterich.**

A New Form of Resistance Thermometer. (By title.) S. **Leroy Brown.**

The Effect of Current and External Heating upon the Elasticity of a Mild Steel and an Aluminum Wire. H. L. **Dodge.**

Isolated Crystals of Metallic Selenium of the Second and Fifth Systems and the Physical Conditions determining their Production. F. C. BROWN.

At a brief business session, the following amendment to By-law No. II. presented October 31st at the New York meeting, was adopted:

"Replace the second sentence of the By-law as it now stands by the following: 'Each new Regular or Associate Member shall pay dues and receive Journals from the January first or July first next following his election.'"

This opportunity is taken of publicly recording the following extracts from the Minutes of the Council, a copy of which was transmitted to Mrs. Peirce in June, 1914, in regard to the death of our late President, B. O. Peirce:

"In view of the universal and genuine grief which has been felt and expressed by the members of the American Physical Society over the death of their late colleague and President, Benjamin Osgood Peirce, the Council of the Society is instructed to make the following minute:

"On the fourteenth day of January, 1914, we lost one of the original group of kindred spirits that banded together for the organization of this Society. His generous and genial personal traits had endeared him to all who knew him. His presence at any meeting went far to make that meeting a happy and successful event. His accurate and profound scholarship was an inspiration to each member. His advice was often sought and always welcomed.

"Remembering Professor Peirce so keenly as a dispenser of sunshine and help, we here make record of our loss. Sharing with his family a deep sense of bereavement, we request our Secretary to send to Mrs. Peirce the warm sympathy of this group of her husband's friends.

"HENRY CREW,
"EDWARD L. NICHOLS,
"ARTHUR GORDON WEBSTER,
"*Committee.*"

On motion, the thanks of the Association were extended to the University of Chicago for arranging Professor Bragg's lecture at the time of our meeting, and for other courtesies extended during the meeting.

A. D. COLE,
Secretary.

SOME FUNDAMENTAL ELECTRO-MECHANICAL, PHOTO-ELECTRICAL AND ELECTRICAL RELATIONS IN CRYSTALS OF METALLIC SELENIUM.[1]

BY F. C. BROWN.

1. Light of all portions of the visible spectrum alters the conductivity of crystals of metallic selenium of two systems.
2. When the light is removed the recovery is very rapid.
3. If the entire crystal is illuminated equilibrium is reached in less than 0.2 second.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 28, 1914.

4. The maximum sensibility for given energy is in the ultra-violet.

5. The crystals are in equilibrium such that a pressure of 180 atmospheres will increase the conductivity a hundred fold.

6. The specific conductivity increases with the applied voltage.

7. The light-action may be transmitted almost undiminished throughout the crystal.

8. The pressure effect is not transmitted outside the region of the mechanical stress in the crystal.

9. The effect of the electric potential is not transmitted beyond the region of the electrical stress, nor does it manifest itself except in the direction of electrical field.

10. The absolute sensibility to light increases with pressure proportional to the conductivity in the dark.

11. This increased sensibility takes place only at the place where the pressure is applied.

12. This increase of sensibility holds for the transmitted light action as well as the direct action of light.

13. The velocity of transmission of the action at a distance by light is greater than two cm. per sec.

State University of Iowa,
Iowa City, Ia.

The Application of the Electron Theory to the Explanation of the Electrical Conduction in Crystals of Metallic Selenium.[1]

By F. C. Brown.

CRYSTALS of metallic selenium are peculiarly adapted for a test of the electron theory of conduction, because of the varied interrelated optical, mechanical and electrical properties. A large number of fundamental experiments have been carried out, which involve large changes in the electrical conductivity.

It is postulated that the nature of the conductivity is the same regardless of the physical conditions that have influenced it. Since the specific conductivity may vary several hundred per cent. by any one of several agencies, it is not conceivable that a variation in the free path or the velocity would sufficiently account for any of the changes. Rather a change in the number of conducting electrons must be expected to account for the varying conductivity.

To merely suppose an addition of free electrons as was first suggested by Pfund,[2] who likened the light-effect in selenium to an internal photoelectric effect is not sufficient. However recent experiments by Sieg and the writer[3] showing a maximum sensibility in the ultra-violet for selenium crystals call

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 28, 1914.

[2] Phys. Rev., Vol. 28, p. 324, 1909.

[3] Phys. Rev., N. S., 1915.

for further efforts to explain light action along the lines suggested by Pfund. The usual free electron hypothesis does not offer an explanation of the increase of light sensitiveness with pressure proportional to the conductivity in the dark. Second it will not explain why the change of conductivity by pressure or electrical fields is limited to the region of the crystal under stress. And third it will not explain why the increase of light-sensitiveness is limited to the region under pressure, and is practically unlimited as to what region of the crystal is illuminated.

The author is proposing a modified form of the electron theory that seems to satisfy all the fundamental experiments thus far recorded.[1] The view supposes that a large portion of the conducting electrons in the crystal are ordinarily fixed in the crystal structure in varying degrees of stability. When an electric field is established across the crystal a certain average number of these fixed electrons are rendered unstable or free. The divergence from the usually accepted notion is that they remain free only for a relatively short interval of time. Thus in these crystals we have the current increasing with voltage more rapidly than required by Ohm's law.

The effect of the increase of pressure is to lessen the degree of the stability so that the mean interval before the recombination of the electrons is increased. Obviously this seems to satisfactorily explain the increased light sensitiveness with increased pressure and the exact proportionality observed, and also the limitation of this increase to the region of the crystal under pressure. The transmitted light action observed by us[2] is probably a mechanical disturbance propagated in the crystal and enters into this theory only as the disturbance keeps electrons out of their fixed positions.

If it were not for this rapid recombination of the electrons the change of conductivity by pressure or electrical forces should be noticable throughout a given crystal structure. A study of the conductivity changes very near the region of applied pressures might give some information as to the rate of recombination of the electrons.

STATE UNIVERSITY OF IOWA,
IOWA CITY, IA.

THE EFFECT OF CURRENT AND EXTERNAL HEATING UPON THE ELASTICITY OF A MILD STEEL AND AN ALUMINUM WIRE.[3]

BY H. L. DODGE.

TESTS upon a sample of mild steel wire over a temperature range of 20° C. to 600° C. indicate a decrease of the Young's modulus at an increasing rate, the total change amounting to about 40 per cent. The nature of the change in the modulus of aluminum wire is the same although the rate of change

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[1] PHYS. REV., N. S., 4, p. 85, 1914, and PHYS. REV. and Phil. Mag. (6), Vol. 28, p. 497.

[2] Phil. Mag., loc. cit.

[3] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 28, 1914.

is much greater. A decrease in the modulus of 40 per cent. occurs with a temperature of about 170° C. Current heating has no effect other than that caused by the accompanying temperature. These results are similar to those secured with copper wire[1] and lead one to believe that further investigation may be expected to lead to the general law that the Young's modulus of metals decreases with increase of temperature at a rapidly increasing rate.

State University of Iowa.

Determination of the Wave-length of Characteristic Roentgen Rays by Means of Diffraction and by the Photoelectric Effect.[2]

By Oscar Alan Randolph.

CHARACTERISTIC Roentgen rays have been isolated from an ordinary Roentgen ray by means of reflection from rock salt, gypsum and brucite, whose spectrograms will be presented. Attempts are being made of measuring the wave-length by 2 independent methods.

University of Illinois,
Urbana, Ill.

Determination of the Elementary Charge of Electricity by Means of Magnetic Properties and the Magneton.[2]

By Jakob Kunz.

A MODIFICATION of the deduction of Langevin's theory of magnetism will first be presented. The average value of e has been found to be $1{,}53.10^{-20}$. Evidence in favor and against the magneton will be discussed. The periodic systems of the elements, their magnetic properties, the magneton and chemical valency will be considered.

University of Illinois,
Urbana, Ill.

The Direct Current Corona of a Wire through a Circular Opening of a Disc.[2]

By L. W. Faulkner.

IN connection with the investigation of S. P. Farwell[3] the corona of a wire through a circular opening in a metallic disc was investigated, in the first place with respect to its practical interest. A large number of interesting phenomena have been observed, especially transient phenomena between two different types of discharge under practically the same conditions as to voltage, pressure, etc. Under a certain pressure of 73 mm. Hg and 4,500 volts when the wire is negative, there appear two beads of light, one travelling up and down

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[1] Phys. Rev., N. S., 2, 431, 1913.

[2] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 28, 1914.

[3] Phys. Rev., 1914, and Proceedings of A. T. E. E.

the wire, the other moving round the circular disc. A large number of characteristic curves and power curves as function of the pressure have been taken. A small arc in series with the discharge tube affects very materially the nature of the phenomena.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

A COMPARISON OF SIMULTANEOUS MEASUREMENTS OF SHORT DISTANCES BETWEEN CONDUCTING FLATS IN AIR, BY THE OPTICAL-ELECTRICAL METHOD.[1]

BY L. E. DODD.

1. Using distances from 28½ to 7 lambda (Na) between conducting flats in air, it has been found that the combined optical and electrical method for measuring short distances (by counting interference bands, and by capacity measurements, respectively) give results showing a linear relationship, the slope of the resulting straight line being 45 degrees, and the line passing through the origin.

2. In the course of the work perfect insulation has been obtained down to seven wave-lengths, with electrodes in air.

3. This method furnishes an invariable determination of the zero point for work between electrodes at small distances, which the work of Rother lacks. In Rother's work the electrodes must first be brought into contact, which condition is assumed when large conduction occurs.

4. The present work differs from Rother's in that he used electrodes in vacua, while here the work has been carried on in air.

5. A possible doubt with regard to the work of Brown has been removed, confirming his results that showed good insulation at as low as two wave lengths of sodium light.

STATE UNIVERSITY OF IOWA,
IOWA CITY, IA.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 28, 1914.

EXPERIMENTAL DETERMINATION OF THE RELATION BETWEEN THE CORONA CURRENT AND THE INCREASE OF PRESSURE DUE TO D.C. CORONA; POSSIBILITIES OF A HIGH VOLTMETER BASED ON THIS PRESSURE PHENOMENON.[1]

BY E. H. WARNER.

IT has been shown by S. P. Farwell that at the instant the corona appears the pressure in the corona apparatus increases. In the PHYSICAL REVIEW, Vol. 4, July, 1914, Mr. Farwell shows the relation of this increase in pressure and the difference of potential.

According to ionization theory the corona current should be directly proportional to this increase in pressure. To test this relation experiments have been performed upon dry air and nitrogen with potential differences up to 15,000 volts. With the wire positive it has been found that the current is directly proportional to the increase in pressure. With the wire negative the relation is direct for lower voltages but with higher voltages the pressure increases more than the current. In this case the currents are larger and therefore the heating effects more prominent. This variation from the direct proportion may be explained by the fact that, in the apparatus used the increase in pressure could not be measured before the current caused a temperature increase which added to the measured pressure increase.

Several attempts have been made to construct a high-potential voltmeter based upon this principle.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

THE LEADING CHARACTERISTICS OF THE ELECTRIC FURNACE SPECTRA OF VANADIUM AND CHROMIUM.[1]

BY ARTHUR S. KING.

A STUDY of these spectra, similar to the previous ones for iron and titanium, has been made with the object of showing at what temperatures the various lines appear and the rate of increase in intensity as the temperature rises, the lines being classified on this basis.

The results show that at a certain temperature, apparently within 200° C. of its melting point, each element begins to show its spectrum, this consisting of a relatively small number of lines which are usually, but not always, among the strongest lines in the arc. At a higher temperature, the bulk of the distinctive arc lines are in evidence, while at the highest temperatures employed with the furnace (2600° to 2700° C.) the main change is in bringing out the weaker arc lines and a widening, with frequent reversals, of the stronger lines. With vanadium, as with titanium, the stronger of the lines peculiar to the spark spectrum are given faintly by the high-temperature furnace.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, November 28, 1914.

In reference to changes in the spectrum with wave-length, lines farther in the ultra-violet are given as the temperature rises, and the arc shows lines of shorter wave-length than the high-temperature furnace. No further resemblance to the intensity change in the spectrum of a solid body with temperature is observable, as low-temperature lines are distributed throughout the spectrum, many of them occurring in the blue and violet.

The tendency of lines to reverse in the furnace spectrum increases toward shorter wave-lengths, reversals being rare in the yellow and red, even among low-temperature lines.

The vanadium spectrum further resembles that of titanium in the large number of lines which are weak in the arc but are given strongly in the furnace. The reason for this is obscure. It appears to be due to differences other than temperature between the arc and the furnace.

The bands occurring in the arc spectra of vanadium and chromium are absent in the vacuum furnace. This indicates that they are probably due to oxides of the metals.

Mount Wilson Solar Observatory,
November 12, 1914.

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PHYSICAL REVIEW.

A DETERMINATION OF LATITUDE, AZIMUTH, AND THE LENGTH OF THE DAY INDEPENDENT OF ASTRONOMICAL OBSERVATIONS.

By Arthur H. Compton.

In a previous paper[1] an experiment was described which afforded a means of measuring the component of the earth's rotation about a vertical axis. Assuming the latitude to be known, the rate of the earth's rotation could then be calculated. The present paper shows how the same method may be employed to measure also the components of the earth's rotation about two mutually perpendicular horizontal axes, so that the rate of the earth's rotation can be determined directly. From the ratio of the vertical component to the resultant rotation the latitude may be found, and from the ratio of the two horizontal components the azimuth may be determined.[2]

If a circular tube filled with liquid is placed in a plane perpendicular to the axis about which the rotation is to be measured, one side of the tube is, in general, moving with respect to the other side. If now the tube is quickly rotated through 180 degrees about an axis in its own plane, the part of the tube on one side of the axis will have its motion changed as it is shifted to the other side, while the liquid retains a large part of its original motion. For example, if a tube bent into a ring of radius r is placed in a plane perpendicular to the earth's axis and is then turned

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[1] A. H. Compton. "A Laboratory Method of Demonstrating the Earth's Rotation," Science, N. S., Vol. 37, p. 803, 1913.

[2] By experiments with an Atwoods machine, such as those conducted by John G. Hagen (John G. Hagen, "How Atwoods Machine Shows the Rotation of the Earth even Quantitatively," International Congress of Mathematics, Aug., 1912) it is theoretically possible to determine the azimuth from the ratio of the deviation of the falling weight toward the south to that toward the east. The earth-rotation ring here described, however, is the only apparatus which has been shown capable of measuring the earth's angular velocity about both vertical and horizontal axes, which is necessary for a determination of the latitude and the length of the day independent of astronomical data.

half way around about a horizontal axis, the upper portion of the tube acquires a relative velocity toward the west when turned to a position nearer the earth's axis than originally equal to $2r\omega$, where ω is the angular velocity of the earth's rotation. The liquid in this part of the tube, however, will retain its original motion, and so will have a relative momentum toward the east. Since the pivots upon which the horizontal axis rests are constrained to follow the earth in its rotation, the component of the motion of the liquid parallel to the direction of the tube at these points is without influence on the relative motion, and only that component of the liquid's momentum which is parallel to the axis will have an effect in producing relative motion when the tube is turned. So if θ is the angular distance of any small portion of the ring from the axis about which it is turned, the mean momentum per unit length of the tube which tends to cause relative motion immediately after the ring is shifted from a position perpendicular to the earth's axis through 180 degrees is:

$$\rho V = 2r\omega\rho \frac{\int_0^{2\pi} \sin^2 \theta d\theta}{\int_0^{2\pi} d\theta}$$

or

$$V = \omega r \tag{1}$$

where ρ is the mass of the liquid per unit length of the tube, and V is the relative velocity between the liquid and the tube.

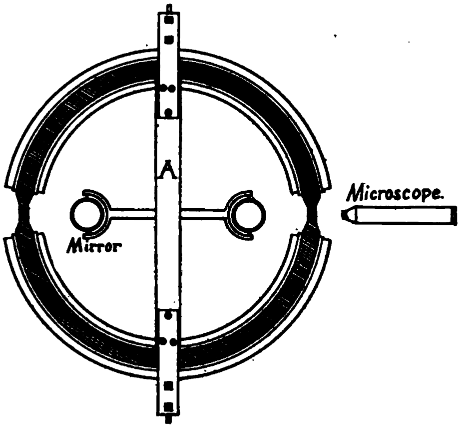

Fig. 1.

Showing the construction of the earth rotation ring.

The ring used to perform this experiment was made of one inch brass tubing bent into a circle eighteen inches in diameter. Where the windows were placed the tube was constricted to a diameter of about three eighths of an inch, as in Fig. 1, so as to increase the velocity of the liquid at the point of observation. In order to prevent convection currents as far as possible, the tube was covered with a quarter of an inch of asbestos, and enclosed in a concentric tin tube with an intervening air space. The protected tube was then mounted on a rigid rod *A* (Fig. 1), the ends of which were made adjustable perpendicular to the plane of the ring, so that the ring might be made to swing upon an axis accurately parallel to its plane. An iron framework was so constructed that the axis could be supported in either a horizontal or a vertical position in order to measure either the vertical or the horizontal components of the earth's rotation.

Carbon disulphide was first used to fill the tube, on account of its low viscosity. Its motion was made visible by shaking up with it an aqueous solution of calcium chloride of the same density, which formed small suspended globules whose motion was easily visible through the microscope. Because of its high coefficient of expansion, however, the convection currents due to slight differences in temperature in different parts of the tube rendered the use of this liquid impracticable. In fact, no liquid could be found whose coefficient of expansion was nearly as low as that of water, so this was finally used to fill the tube. A mixture of coal oil and carbon tetrachloride was prepared of the density of water at 4° Centigrade, at which temperature most of the measurements were made. The slight change in relative density due to a rise to room temperature did not noticeably affect the motion of the smaller globules of the oil when shaken up in the water.

When the ring was held in a horizontal plane, no particular pains were required to eliminate convection currents, since the only time that a difference in density in different parts of the tube could affect the motion of the water was while it was being turned over. When the ring was held in a vertical plane, however, in order to measure the horizontal components of the earth's rotation, the slightest variation in density in different parts of the tube was immediately noticed. Great precautions were taken to keep the ring at uniform temperature throughout. The whole apparatus was enclosed in an asbestos box, and the within was stirred by an electric fan, as in Fig. 2. A further asbestos shield prevented the observer's breath from striking the enclosing box, and the surrounding air was kept well stirred by an electric fan. By this means the difference in temperature of different parts of the tube was kept within 0.05 of a degree, but even this small difference at ordinary room temperature produced convection currents comparable in magnitude with the motion of the water due to the earth's rotation. In order to eliminate still further these currents, the apparatus was set in a constant temperature room and kept at 4° Centigrade by means of a thermostat. In this manner it was found possible to eliminate almost entirely the effect due to the convection currents.

In taking a reading, a microscope with an eye-piece scale was focused on the center of the tube under the glass window, and the ring was held in position until the oil globules had no appreciable motion. The ring was then quickly turned over, and the number of scale divisions passed by the globules between the fifth and fifteenth seconds after the ring was reversed was noted. A telegraph sounder actuated by the laboratory clock was used to measure the time during which the motion was followed. Immediately after the ring was turned over there was a large motion across the tube, but this soon died out, and the motion along the tube could be accurately measured.

TABLE I.

Reading Given in Scale Divisions.

	Case *A*.	Case *B*.	Case *C*.	Case *D*.
Setting I.	+13	+25	+10	+24
Axis vertical, Ring Approx.	+12.5	+25	+11	+24.5
ENE×WSW.	+14.8	+20.5	+13.8	+17.5
Ave. 9 r'd'gs:	+15.35	+21.19	+13.42	+19.71
X_1 = Average of 4 cases = + 17.41 divisions.				
Setting II.	− 7	−10	−14	− 8
Axis vertical, Ring approx.	− 8.2	−13	−14	− 7.5
NNW×SSE.	−10	− 9.5	− 9	− 6.5
Ave. 10 r'd'gs:	− 9.70	− 9.59	−12.33	− 6.60
X_2 = Average of 4 cases = − 9.55 divisions.				
Setting III.	+14.5	+ 8	+19.5	+17.5
Ring horizontal.	+35	+20	+11	+30
	+10	+24	+32	+12
Ave. 10 r'd'gs:	+15.35	+18.20	+23.15	+17.10
X_3 = Average of 4 cases = + 18.42 divisions.				

Some typical readings thus obtained with the ring set in the three mutually perpendicular planes are shown in Table I. The four cases, *A*, *B*, *C*; *D*, represent the four different ways in which the ring may be turned. By taking the average of these four cases, differences in the readings due to slight convection currents and to inaccurate adjustment of the axis about which the ring is turned cancel out. The positive

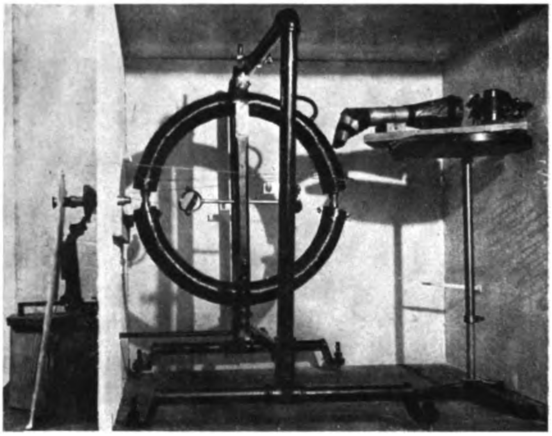

Fig. 2.

Measuring a horizontal component. One side of enclosing box removed to show apparatus within.

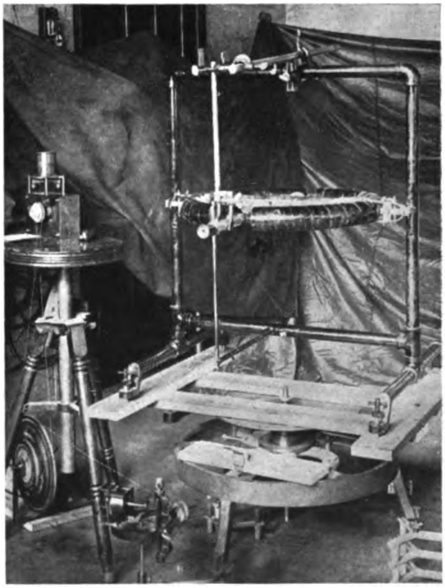

Fig. 4.

Absolute determination of horizontal component of earth's angular velocity.

ARTHUR H. COMPTON.

direction is taken as upward as seen in the microscope (a real downward motion) in the first two settings, and toward the right in the third. In the first setting observations were taken on the west side of the ring, and the fact that the water was moving relatively downward on this side after the ring was reversed indicates that the earth is revolving from west to east. Similarly the relatively upward motion observed on the east side in the second setting indicates the same sort of motion. The third setting showed a relative motion to the left on the side of the ring observed, which shows a rotation of the earth in a counter-clockwise direction about a vertical axis. Thus qualitatively the rotation of the earth about the three different axes is shown.

$$\varphi = \text{latitude} = \sin^{-1}\frac{X_3}{\sqrt{X_1^2 + X_2^2 + X_3^2}} = 42.8^\circ.$$

$$\psi = \text{azimuth} = \tan^{-1}\frac{X_2}{X_1} = 28.7^\circ.$$

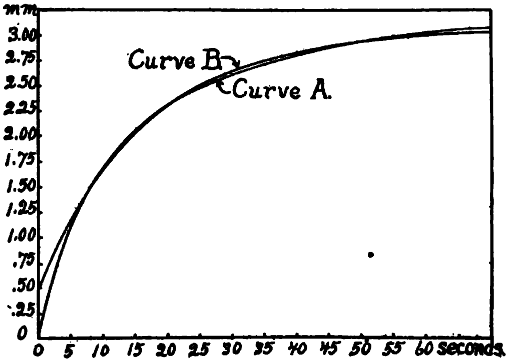

Fig. 3.

In order to make an accurate estimate of the angular velocity corresponding to any observed motion, it is necessary to find the law of motion of the water in the tube. If the motion were uniform the resistance would be proportional to the velocity, as assumed in the previous paper,[1] but this is not exactly true when the velocity changes with the time, if the motion of the water at the center of the tube be considered. For instance if the water in the tube is given an impulsive motion, immediately after the impulse the resistance at the center of the tube is zero, while the velocity is a maximum. However, if the greater part of the resistance occurs at definite points in the tube, as in the ring used in this experiment, the above law will hold more accurately than for a tube of

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[1] Ibid., p. 805.

uniform diameter. An experimental test of the accuracy of this law for a uniform circular tube is afforded by a comparison of the curves A and B in Fig. 3, taken from my previous paper. Here curve A represents the motion of the water as determined by a large number of readings, while curve B represents the motion as it would be if the resistance were proportional to the velocity, showing a rather close agreement. We shall assume, therefore, that for our present purposes the resistance may be considered proportional to the velocity, that is:

$$\frac{d^2x}{dt^2} + c\frac{dx}{dt} = 0,$$

where x is the distance travelled along the tube, t is the time, and c is a constant depending upon the viscosity and density of the liquid and the dimensions of the tube. The solution of this equation may be put in the form:

$$X = \frac{V}{c}(e^{-ct_1} - e^{-ct_2}),$$

where X is the distance through which the motion of the water is followed, V is the initial velocity of the water after the ring is turned over, t_1 is the time of beginning, and t_2 that of ending the observation of the motion of the globules. Since in all the readings the times t_1 and t_2 were taken the same, the initial velocity of the water V is proportional to the distance X through which its motion is followed. But by equation (1)

$$V = \omega r,$$

so that X is proportional to ω, that is, the distance through which the water is followed is a measure of the component of the angular velocity about an axis perpendicular to the plane of the ring. Thus if we let α be the factor of proportionality,

$$\omega = \alpha X. \qquad (2)$$

Let ξ, η, and ζ be the components of the earth's angular velocity about axes perpendicular to the plane of the ring in settings I., II. and III. respectively, and X_1, X_2, X_3 be the average motions observed in the three settings. Then by equation (2)

$$\xi = \alpha X_1; \; \eta = \alpha X_2; \; \zeta = \alpha X_3.$$

If we call φ the latitude and ψ the angle between the ξ axis and the north, then from Table I.:

$$\left.\begin{aligned} \xi &= \omega\cos\varphi\cos\psi = +17.41\,\alpha, \\ \eta &= \omega\cos\varphi\sin\psi = -9.55\,\alpha, \\ \zeta &= \omega\sin\varphi \qquad\quad\; = +18.42\,\alpha, \end{aligned}\right\} \qquad (3)$$

from which

$$\begin{aligned} \omega &= 27.08\,\alpha, \\ \sin\varphi &= 0.680, \\ \varphi &= 42.8^\circ = \text{latitude}, \\ \tan\psi &= 0.548, \\ \psi &= 28.7^\circ = \text{azimuth}. \end{aligned}$$

A quantitative determination of the absolute magnitude of the earth's angular velocity from these data may be made if the constant α in equation (2) is evaluated. An attempt was made to determine this constant by placing the ring on a spectrometer table which was turned at the desired angular velocity by means of a driving clock. The ring was turned with known angular velocity until the motion of the ring became uniform, and was then stopped under the microscope, and the motion of the water observed. The constant as determined in this way is not strictly comparable, however, with that which enters when the ring is turned over just before the motion of the water is observed. It was found necessary, therefore, to use a different method for calibrating the tube.

The method employed was a direct determination of the angular velocity of the vertical component of the earth's rotation. This was done by placing the whole apparatus upon the table of the spectrometer, as shown in Fig. 4. The table was rotated by means of the driving clock at such speed that the readings taken on reversing the ring with the clock running were approximately equal but opposite in sign to those taken when the clock was stopped. So if X_4 be the observed motion of the water when the clock was stopped and X_4' that when running, the vertical component of the earth's angular velocity is

$$\zeta = \frac{-\chi}{\left(1 - \dfrac{X_4'}{X_4}\right)},$$

where χ is the angular velocity at which the spectrometer table was turning. As shown in Table II., the readings for determining X_4 and X_4' were taken in alternate sets of four, one under each of the four cases, every other set being made with the clock running. In this manner all systematic errors were eliminated, so that the accuracy with which X_4 and X_4' can be determined is a direct function of the number of readings taken. It may be noted that although X_4 and X_3 are both measures of the earth's rotation about a vertical axis, the two quantities are not directly comparable, since the temperature at which X_4 was measured

Table II.

Apparatus on Spectrometer Table. Readings in Scale Divisions.

Case *A*.		Case *B*.		Case *C*.		Case *D*.	
Clock: Off.	On.	Off.	On.	Off.	On.	Off.	On.
+24		+37		+38		−12	
	−22		−10		−24		−63
+38		+49		+21		+16	
	−49		−22		−17		−34

Average X_4 (28 readings) = + 27.5 divisions.
Average X_4' (28 readings) = − 29.9 divisions.
χ = angular velocity of spectrometer table relative to earth
= − 3° in 512.4 sidereal seconds,
= − 0.00585 degrees/second.
ζ = vertical component of earth's angular velocity.

$$= \frac{-\chi}{\left(1 - \frac{X_4'}{X_4}\right)} = 0.673 \text{ revolutions/day.}$$

ω = earth's angular velocity.

$$= \frac{\zeta}{\sin \varphi} = 0.991 \text{ revolutions/day.}$$

was some twenty degrees higher than that for X_3, and the viscosity was correspondingly less. The quantity χ was measured directly, and was found to be − 0.00585° per sidereal second. Substituting the values of X_4 and X_4' as obtained in Table II., the vertical component of the earth's angular velocity becomes:

$$\zeta = \frac{0.00585}{\left(1 + \frac{29.9}{27.5}\right)}$$

$$= 0.00280 \text{ degrees/second,}$$

$$= 0.673 \text{ revolutions/day.}$$

But by equation (3)

$$\zeta = + 18.42\,\alpha,$$

so that

$$\alpha = 0.03656$$

and

$$\omega = 0.991 \text{ revolutions/day.}$$

The length of the day is therefore 24 hours 12 minutes in sidereal time.

These values of ω, φ and ψ may be compared with their values as determined astronomically thus:

By Data from Earth-Rotation Ring.	By Astronomical Data.	Difference.
ω = 0.991 revs/day	1.000 revs/day	0.9%
φ = 42.8°	40.4°	2.4°
ψ = 28.7°	30.1°	1.4°

The remarkable agreement of the two values of ω is only accidental, since if the true value of φ is used in determining ω by data from the earth-rotation ring,

$$\omega = \frac{\zeta}{\sin\varphi} = \frac{0.673}{0.650} = 1.034 \text{ revs./day},$$

which represents a difference of 3.4 per cent. Although the comparatively low degree of accuracy of these data renders them valueless for work which requires precision, it is interesting to find that these quantities can be determined without reference to astronomical observations.

In conclusion I wish to thank Professor Russell of the Department of Astronomy for his suggestions, and Professor Magie for his kind encouragement in carrying on this experiment.

Palmer Physical Laboratory,
Princeton, N. J.
November 3, 1914.

APPLICATION OF A THEORY OF IONIZATION BY IMPACT TO THE EXPERIMENTS OF FRANCK AND HERTZ.

BY BERGEN DAVIS.

THE energy of ionization by impact of the various gases, that is, the energy required to separate an electron from a molecule, is an important constant in all theories of the discharge of electricity through gases. A number of investigators have attempted to determine the ionization voltages of the various gases, but the results obtained differ so widely among themselves that one cannot regard this constant as fixed with any degree of accuracy.

It has been shown by Professor J. S. Townsend[1] that the experimentally determined values of the ionizing impacts per cm. α at any pressure p and any electrical intensity X, could be plotted on a single curve in which the abscissæ were the values of X/p and the ordinates were α/p. That is, for all conditions, α/p is a function of X/p:

$$\frac{\alpha}{p}=f\left(\frac{X}{p}\right).$$

He[2] has recently derived an expression for this functional relation and has applied it to his experimental data for the calculation of the least voltage of ionization by impact. The values so calculated range from 23 to 29 volts. The results are not constant, and also they are greater than those obtained by other methods and also by direct experiment. This lack of constancy is probably due to the fact that his equation is not a complete expression for the relation between a, p and X.

Dr. E. S. Bishop[3] has applied to his own experimental results, a theory of ionization by impact developed by the writer,[4] and obtains the constant value of 10.2 volts as the ionization voltage of air.

However, all of these methods of determining the ionization voltage are indirect. An interesting direct method has recently been employed by Franck and Hertz.[5] There can be but little doubt that this direct

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[1] Phil. Mag., Feb., 1901.

[2] Phil. Mag., Feb., 1914.

[3] PHYSICAL REVIEW, November, 1911.

[4] PHYSICAL REVIEW, January, 1907; Annal. d. Physik, Band 42, 1913.

[5] Ber. d. D. Phys. Ges., Heft 2, 1913.

method gives a more correct value of the ionization voltage than any of the indirect methods that have been employed. They have also added an interesting and fruitful idea to our conceptions of ionization by impact, namely, that in certain gases, the impacts are wholly or in part non-elastic, and in other gases the impacts are nearly or quite elastic. In general the noble gases (neon, helium) exhibit the phenomenon of elastic impact, while on the other hand, the gases that form chemical compounds readily (hydrogen, nitrogen, oxygen) behave as though the impacts were non-elastic.

The same experimenters[1] have investigated the ionization voltages for nitrogen and oxygen, with a specially designed apparatus which gives no current until the ionization voltage is reached. The current then increases rapidly with an increase of the applied voltage.

The purpose of this paper is to develop a theory of the current curves for this apparatus in the case of non-elastic impact and to compare it with the experimental results.

THEORY OF THE CURRENT CURVES.

The following assumptions are made: (*a*) The impacts are non-elastic, that is, an electron loses all of its velocity at collision with a molecule, and starts again from rest with an acceleration due to the applied electric field: (*b*) There is a certain minimum voltage ($v_0 = X\lambda_0$) below which ionization by impact can not occur: (*c*) Not every impact in which the electron has had a free run through a voltage $X\lambda_0$ results in ionization, but only a fraction of them do so. Only a small part of those ions whose paths are λ_0 result in ionization, but those that make paths $(\lambda_0 + x)$ are more effective in producing ions. The fraction of all the impacts having paths greater than $(\lambda_0 + x)$ that produce new ions is $x/(\lambda_0 + x)$, where λ_0 is the least ionizing path, and x is some path additional to λ_0. The fraction thus depends on the length of path of the ion, that is, on its energy at the moment of impact.

The derivation[2] of this fraction depends on the fundamental consideration that the effective form of a molecule is spherical, and that the *normal component* of the momentum of the ion at impact with a molecule shall be equal to or exceed a certain constant fixed value. An ion striking a glancing blow must, to be effective, possess more energy than one which strikes the molecule centrally.

The experimental arrangement used by Franck and Hertz may be schematically represented by Fig. 1, in which A is the source of the nega-

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[1] Ber. d. D. Phys. Ges., Heft 2, 1913.

[2] PHYS. REV., Jan., 1907; Annal der Phys., Band 42, 1913.

tive ions, B is a wire mesh or grid, and D is a plate electrode. The ions are accelerated by the field applied at AB, and are slowed up by a reverse field applied to BD. Some of the negative ions from A pass through the grid B and cause ionization by impact in the region BD. For the sake of simplicity, it will be assumed that these ions from A derive all their energy from the field on AB, and that the field on BD is just equal and opposite to the field on AB. Those ions passing through the grid B and not making impact will just lose their velocity before reaching D, and will fall back to B. The quantity measured is the positive ionization produced in region BD by the ions that pass through B. *These* positive ions are driven to the plate D which is connected to an electrometer. Two cases will be treated separately.

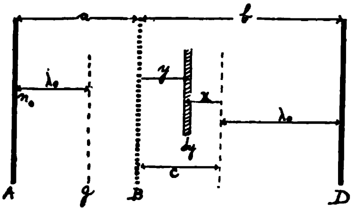

Fig. 1.

Case I.—The ionization in BD is due to the impact of the original n_0 ions starting from A.

Case II.—The ionization in BD is due to the impacts of the *new ions* produced in AB, upon *their* passage through the grid B.

Case I.—The usual laws of the kinetic theory of gases will be applied to the motion of the ions through the gas. The development becomes quite simple by reference to the figure.

Let A be the source of the n_0 ions (electrons) which acquire a velocity from the field on AB. Some of these ions pass through the grid B. The grid B will be considered a mathematical plane in the gas. The wires of the mesh have no dimensions and do not of themselves stop any of the ions. These ions have a velocity sufficient to cause ionization as they go beyond B, but if they do not make impact in a short distance, they lose their excess velocity on account of the reverse field on BD. How far they go before losing their excess energy depends on the value of the potential v applied to AB and BD.

In the figure, λ_0 is the least ionizing path, and $v_0 = X\lambda_0$ is the least ionizing voltage. The distance from A to B is denoted by a, and the distance BD by b.

The ionization by impact of which we need take account will take place in a distance C in region BD. The ionization produced in region gB need not be considered, since these positive ions cannot reach the plate D.

Let n_0 be the number of negative ions (electrons) escaping from A per unit of time. The number going beyond $(a + y)$ without impact are

$$n_0 e^{-\frac{a+y}{l}}$$

and those making impact in a space dy beyond $(a + y)$ are

$$n_0 e^{-\frac{a+y}{l}} \frac{dy}{l}.$$

Not every impact, however, produces a new ion, but a fraction of them do so. This fraction, whose derivation is referred to in a previous paragraph, is $x/(\lambda_0 + x)$.

The new ions produced in dy will be

$$n_0 e^{-\frac{a+y}{l}} \frac{x}{\lambda_0 + x} \frac{dy}{l},$$

and consequently

$$n_1 = n_0 \int_0^c e^{-\frac{a+y}{l}} \frac{c - y}{b - y} \frac{dy}{l}. \qquad (1)$$

By integration, this becomes:

$$\frac{n_1}{n_0} = e^{-\frac{a}{l}} - e^{-\frac{a+c}{l}} - \frac{b - c}{l} e^{-\frac{a+b}{l}} \left\{ Ei\left(\frac{b}{l}\right) - Ei\left(\frac{b - c}{l}\right) \right\}. \qquad (2)$$

An inspection of the figure shows at once that $c = b - \lambda_0$, also that $v = Xa = X'b$, and $v_0 = X\lambda_0$, where X is the electrical intensity and v is the applied voltage. The substitution of these quantities in (2) gives

$$\frac{n_1}{n_0} = e^{-\frac{a}{l}} - e^{-\frac{a}{l}\left(\frac{2v - v_0}{v}\right)} - \frac{b}{l}\frac{v_0}{v} e^{-\frac{a+b}{l}} \left\{ Ei\left(\frac{b}{l}\right) - Ei\left(\frac{b}{l}\frac{v_0}{v}\right) \right\}. \qquad (3)$$

The form of the current curve is expressed in terms of the applied voltage and the dimensions of the apparatus. It will be compared to the experimental current curves obtained by Franck and Hertz. Their apparatus consisted of a hot wire source of ions (electrons) A, a cylindrical wire grid B, and a cylindrical electrode D surrounding B. The distance a was .5 cm., and distance b was 3 cm. The observations were made at a pressure of .02 mm. of Hg.

In calculating equation (3) the mean free path of a negative ion is taken at eight times the mean free path of a molecule at the pressure considered. This value, rather than the ratio $4\sqrt{2}$ was taken for the following reasons: (a) An expression derived by the writer[1] for the functional relation

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right)$$

is found to agree closely with all of the experimental results of Professor Townsend if one takes the mean path of an ion as about eight times that

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[1] Annalen der Physik, Band 42, 1913.

of the molecule. It does not agree for any other value of the mean free path. The fundamental basis of the theory of this paper and also that employed in deriving the expression just referred to, is the same, so it is necessary to use about the same value for the mean free path of the ion in the two cases. (*b*) Recently Partzsch[1] has applied a modification of the equation of Townsend to his own investigation of the relation between the pressure, voltage and current in a gas. A good agreement is found to obtain when the mean free path of an electron is taken eight times that of a molecule.

In nitrogen at .02 mm. pressure $l = 8L$ equals 3.04 cm., and in oxygen $l = 8L$ equals 3.25 cm. at the same pressure. The values of v_0 found by Franck and Hertz were 7.5 volts for nitrogen and 9 volts for oxygen. The plotted curves for equation (3) are shown by the full lines in Fig. 2.

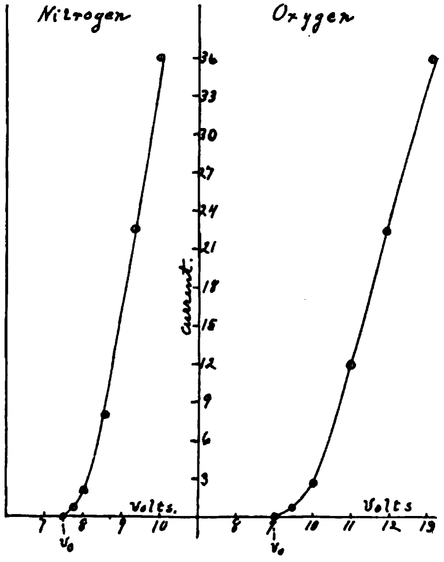

Fig. 2.

The dotted circles represent the experimental current curves obtained by Franck and Hertz.

The very good agreement here shown would indicate that the assumptions made in the development of the theory are fairly well justified, and it may be concluded that the impacts in nitrogen and oxygen are approximately non-elastic.

Case II.—The ionization in *BD* is due to the impact of the ***new ions*** produced in *AB* upon ***their*** passage through the grid *B*.

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[1] Annalen der Physik, Band 40, 1913.

The total current curve will be considered as composed of two parts, n_1 and n_2. The part n_1 represents the plot of equation (3) for all values of v from v_0 to $3v_0$. It represents the ionization produced by the original ions from A. As the voltage is increased beyond $2v_0$, some of the new ions formed in region AB possess the necessary ionizing energy when they pass through B. The part n_2 represents only the ionization in BD due to these new ions from AB.

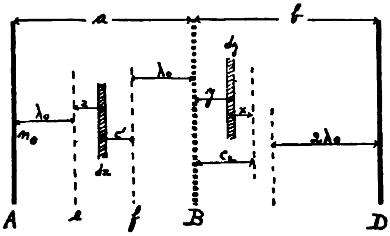

Fig. 3.

In the case of nitrogen and oxygen Franck and Hertz did not determine the current at voltages equal to or greater than $2v_0$. However, it will be interesting to investigate the form of the current curves at higher voltages, as it probably gives a method of distinguishing directly whether a gas exhibits the phenomena of elastic or non-elastic impact.

The method of deriving the equation for the current curve n_2 is similar to that of Case I. The development can be readily followed by reference to the figure.

The n_0 ions from A set free by impact new ions in the region AB. Only those that are produced in region ef, however, need be considered, since no new ions are formed in region Ae, and those ions set free in region fB have not the requisite energy on their passage through grid B. The ionization in region ef is thus a new source of ions. The extent of region ef depends on the applied voltage. When $v = 2v_0$, the planes e and f coincide. When $v = 3v_0$, the distance between the planes e and f becomes equal to λ_0.

Let dz be an element of the region ef. Some of the ions set free in dz will pass through B and cause ionization in BD as far as c_2. Their excess energy disappears beyond c_2 because of the reverse field on BD. The region dz becomes now a new source of ions whose ionizing action may be treated as in Case I.

The new ions set free in dz will be

$$dn' = n_0 e^{-\frac{\lambda_0+z}{l}} \frac{z}{\lambda_0 + z} \frac{dz}{l}. \tag{4}$$

The same reasoning applied to these dn' ions as to the n_0 ions from A in Case I gives

$$dn_2 = dn' \int_0^{c_2} e^{-\frac{\lambda_0+c'+y}{l}} \frac{c_2 - y}{\lambda_0 + c_2 - y} \frac{dy}{l}. \tag{5}$$

By reference to Fig. 3 it will readily be seen that

$$c_2 = \frac{b}{a}c', \quad \text{and that} \quad c' = a - 2\lambda_0 - z.$$

The complete integral equation is thus obtained

$$\frac{n_2}{n_0} = \int_0^{a-2\lambda_0} e^{-\frac{\lambda_0+z}{l}} \frac{z}{\lambda_0 + z} \frac{dz}{l} \times \int_0^{\frac{b}{a}(a-2\lambda_0-z)} e^{-\frac{(a-\lambda_0-z)+y}{l}} \frac{\frac{b}{a}(a - 2\lambda_0 - z) - y}{\frac{b}{a}(a - 2\lambda_0 - z) + \lambda_0 - y} \frac{dy}{l}. \tag{6}$$

The second integral term of (6) is the same as that of equation (1). It may be directly written down.

$$\frac{n_{2_1}}{n_0} = \int_0^{a-2\lambda_0} e^{-\frac{\lambda_0+z}{l}} \frac{z}{\lambda_0 + z} \frac{dz}{l} \left[e^{-\frac{a-\lambda_0-z}{l}} - e^{-\frac{a-b+\lambda_0\left(1+\frac{2b}{a}\right)-z\left(1+\frac{b}{a}\right)}{l}} - \frac{\lambda_0}{l} e^{-\frac{a+b-\frac{2b}{a}\lambda_0-z\left(1+\frac{b}{a}\right)}{l}} \left\{ Ei\left(\frac{\lambda_0 + \frac{b}{a}(a-2\lambda_0-z)}{l}\right) - Ei\left(\frac{\lambda_0}{l}\right) \right\} \right]. \tag{7}$$

The direct integration of the variable z in the exponential integral term of (7) would be a matter of great difficulty. A graphical method of

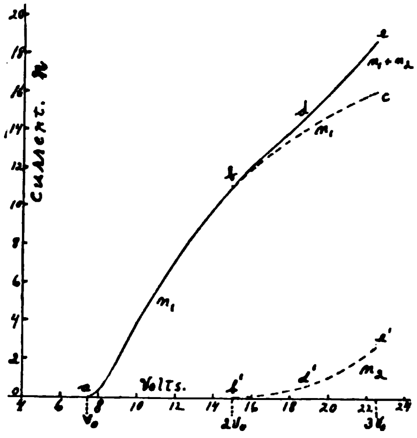

Fig. 4.

integration was used instead. Although equation (7) contains any desired dimensions (a and b) of the apparatus, for the sake of reducing the labor of calculation somewhat, I have taken $b = a$ equal to one centimeter.

The broken line $b'd'e'$ of Fig. 4 represents the results of the graphical integration of equation (7). The curve *abc* represents equation (3) for n_1 over a voltage range from v_0 to $3v_0$. The total current indicated by the electrometer connected to D will be $n = n_1 + n_2$, and is represented by the curve *abde*.

The lack of experimental data on the form of the current curves for this design of apparatus at voltages greater than $2v_0$, prevents a complete checking of the theory. However, there is a very good agreement over that voltage range employed by Franck and Hertz. This agreement supports the assumptions made in this paper and indicates that the impacts in nitrogen and oxygen are nearly or quite non-elastic.

Phoenix Physical Laboratory,
Columbia University,
October, 1914.

A NEW FORM OF RESISTANCE THERMOMETER.

BY S. LEROY BROWN.

THE metallic oxides are generally considered to be non-conductors of an electric current. At room temperature or lower they are very poor conductors, but at higher temperatures most oxides can be considered as conductors. The resistance of powdered forms of several oxides at temperatures as high as 1100° C. has been investigated by Mr. A. A. Somerville,[1] and his results show that a specimen of copper, iron or zinc oxide may reduce its resistance from several million ohms at room temperature to a few hundred ohms at 1000° C. The determination of the resistance of a powdered specimen or a solid form which has been obtained by baking the powdered specimen, must necessarily give results which are only applicable to the particular sample under test, since much must depend on the compactness obtained in each case.

The object of this paper is to give the results of the determination of the resistance of oxides which have been melted and molded into solid rods, and to show the application of their resistance-variation with temperature as resistance thermometers.

Solid rods were obtained by filling porcelain tubes with powdered or solid forms of the oxides and melting the oxide by placing the tubes in a tubular electric furnace. By packing a porcelain tube which is 12 or 15 inches long with powdered copper oxide, melting the oxide, and allowing it to cool and harden, a solid rod can be obtained 5 or 6 inches long and 3/8 of an inch in diameter. The sample can be used encased in the porcelain, which affords some protection, or the porcelain may be ground away on an emery-wheel and the bare solid oxide obtained.

The large temperature coefficient of resistance of the metallic oxides suggested their possible value as resistance thermometers when properly made and used. The solid rods which were obtained from the molten states of some of the oxides are very hard and strong, so that their resistances are not changed by mechanical jars or small changes in pressure. The results show that a resistance thermometer can be made with a metallic oxide as the element which will withstand very rough heat treatment and any reasonable mechanical treatment, and still retain the

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[1] Metallurgical and Chemical Engineering, Vol. X., No. 7, p. 422, July, 1912.

same electrical resistance at a particular temperature. Several months' use of such a thermometer with iron oxide as the element showed that many reheatings to temperatures ranging from 100° C. to 500° C. failed to cause any measurable change in its resistance.

The principal difficulty in the resistance measurements is caused by poor and variable contact resistance where the metal leads are connected to the oxide. It is impossible to solder the connecting wires to the oxides, although the solder will cling to some of them and apparently make good connections; but such connections were never found to be free from a variable contact resistance. Satisfactory connections were made by clamping two pairs of leads against the ends of the oxide element, and the potentiometer method of measuring its resistance was used. The one pair of leads carried the exciting current and the other pair were the potential leads, which were connected to the potentiometer as indicated in Fig. 1. The variable contact resistance between the oxide and the exciting-current leads is thereby eliminated if a potentiometer balance is made with the standard resistance immediately after each balance is obtained with the oxide element.

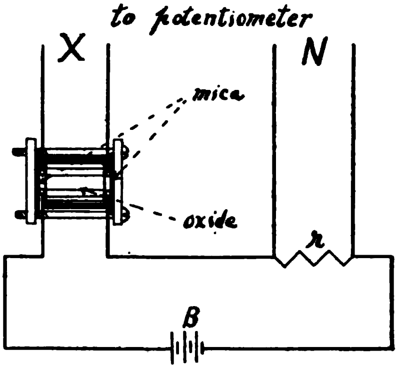

Fig. 1.

The solid copper oxide elements, with which the following data were obtained, were formed by filling a porcelain tube with cupric oxide and heating to about 1400° C. in an electric furnace. At this temperature the CuO reduces to Cu_2O. The melted cuprous oxide was withdrawn from the furnace and quickly cooled. Chemical analysis of the solid formed showed it to be about 98.7 per cent. cuprous oxide.[1] If cuprous oxide is maintained at about 800° C., it will decompose into cupric oxide and free copper. Evidently the rapid cooling accounts for the very small per cent. of cupirc oxide in these specimens. One resistance element was formed in the above described manner, then heated to 800° C. and allowed to cool slowly. The cuprous oxide decomposed into cupric oxide and free copper and the resistance of the element was reduced from about 60,000 ohms at 26° C. to about 4,100 ohms at the same temperature. A rise of temperature would decrease the resistance of the element, which then consisted of a mixture of cupric oxide and

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[1] The author is indebted to Mr. D. J. Brown of the school of chemistry, The University of Texas, for the analyses of these oxides.

copper; but its resistance would be higher than originally when its temperature was reduced to the original temperature. Of course this variation in its resistance made it worthless as a resistance thermometer. This means that the upper limit of the cuprous oxide resistance thermometer is certainly under 800° C.

The solid iron oxide elements were made by filling a porcelain tube with ferric oxide, heating to about 1550° C. and then allowing to cool. The melting of the ferric oxide caused a reduction to magnetite (Fe_3O_4), and therefore the sold elements which were used as iron oxide resistance elements are solid magnetite. Chemical analysis showed the solid to be magnetite.

The solid lead oxide was obtained by melting the powdered lead oxide in an electric furnace in the same manner as described for the copper and iron oxide.

Short elements with comparatively large cross-sections can be made which have only a moderate resistance at room temperature, and small heat capacity. Iron oxide (Fe_3O_4) and cuprous oxide (Cu_2O) gave the most satisfactory results (as far as the author's investigation was extended) for temperatures ranging from a few degrees below zero to 400 or 500 degrees centigrade, although lead oxide (PbO) can be used very satisfactorily between 100 and 600 degrees centigrade. The lead oxide is more brittle than either iron or copper oxide, and therefore is easily cracked or chipped. The extremely high resistance of lead oxide at room temperatures necessitates a very thin element in order that its resistance be not prohibitive.

The accompanying data and curves show the temperature variation of resistance for the three oxides and the sensibility of an iron oxide resistance thermometer at several temperatures. The sensibility at a particular temperature is expressed as the change in resistance per degree per unit of resistance at the particular temperature; that is, the sensibility at a particular temperature is the slope of the temperature-resistance curve at that temperature, divided by the resistance at that temperature. The sensibility of these thermometers is very much higher at low temperatures, but they are sufficiently sensitive at high temperatures to warrant their use.

OXIDE RESISTANCE THERMOMETER NO. 1.

Description.—The resistance element of this thermometer consists of a cylindrical piece of cuprous oxide (Cu_2O) encased in a porcelain tube in which cupric oxide had been melted. The length of the element is .6 of a centimeter and its diameter is .8 of a centimeter.

The resistance measurements for all the data in this paper were made with a Wolff potentiometer, and connections were made to the oxide as shown in Fig. 1. For all temperatures up to 200° C., the resistance thermometer was placed in a uniformly heated oil bath and the temperatures measured with a standardized mercurial thermometer. The higher temperatures were obtained by a tubular electric furnace and measured with a standardized platinum, platinum-iridium thermo-couple.

Table I.

Temperature.	Resistance.	Temperature.	Resistance.
− 3.2° C.	83,750	96° C.	4,943
.2 "	71,600	117.5 "	3,820
.6 "	70,250	130.1 "	3,220
1.9 "	66,750	146 "	2,610
8.4 "	49,650	162 "	2,043
16 "	36,100	185 "	1,521
27.3 "	23,500	198 "	1,285
28.5 "	22,550	221 "	1,012
34.2 "	17,000	251 "	770
45 "	12,200	281.5 "	615
58 "	8,515	327 "	438
81 "	5,920	375 "	319.2

The heavy curves in Fig. 2 show the resistance variation with tem-

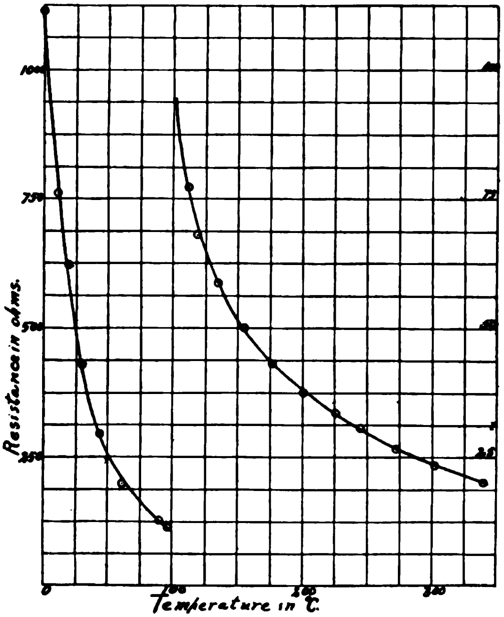

Fig. 2.

perature for cuprous oxide. The scale on the right margin refers to the curve which pertains to temperatures higher than 100° C.

OXIDE RESISTANCE THERMOMETER NO. 2.

Description.—The element of this thermometer is similar to the element of No. 1 except it is 9.35 centimeters long.

TABLE II.

Temperature.	Resistance.	Temperature.	Resistance.
0° C.	8,915,000	29.42° C.	2,678,300
1 "	8,490,000	30.22 "	2,610,000
2.5 "	7,840,000	30.92 "	2,560,900
9 "	6,452,000	34.2 "	2,090,000
17.5 "	4,448,000	45 "	1,498,000
22 "	3,585,000	58 "	1,048,000
27.2 "	2,922,000	75 "	749,000
28.5 "	2,772,000	89.8 "	568,000

The dotted curve in Fig. 2 shows a graph of the above data if the scale at the left margin is multiplied by 100.

OXIDE RESISTANCE THERMOMETER NO. 3.

Description.—The element of this thermometer consists of a solid piece of lead oxide (PbO) which is .7 of a centimeter long and about .75 of a centimeter in diameter. The cross-section is not quite uniform.

TABLE III.

Temperature.	Resistance.	Temperature.	Resistance.
52° C.	4,285,000	116° C.	124,900
60 "	3,535,000	120 "	102,600
68 "	2,760,000	136 "	57,800
76 "	1,998,000	149 "	37,800
81 "	1,510,000	168 "	23,550
91 "	762,500	184 "	12,510
94 "	466,000	202.5 "	6,175
97.7 "	368,500	230 "	3,711
110 "	191,000	259 "	1,468

The curves in Fig. 3 show the resistance variation with temperature for lead oxide. The scale at the right margin refers to the curve which pertains to temperatures higher than 100° C.

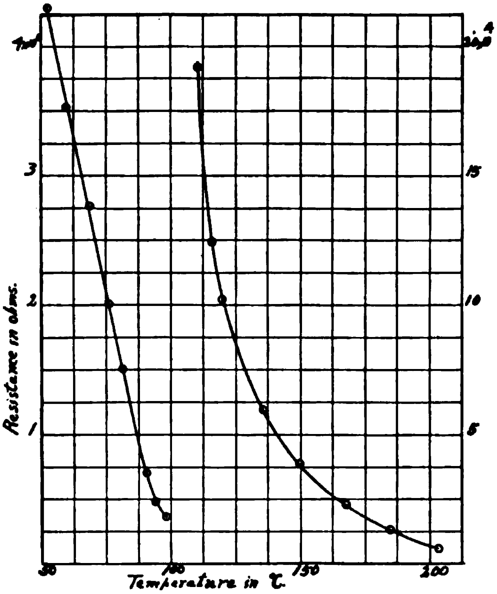

Fig. 3.

Oxide Thermometer No. 4.

Description.—The resistance element of this thermometer consists of a cylindrical piece of solid magnetite (Fe_3O_4) which was obtained by melting powdered iron oxide (Fe_2O_3). The length of this element is .85 of a centimeter and its diameter is .65 of a centimeter.

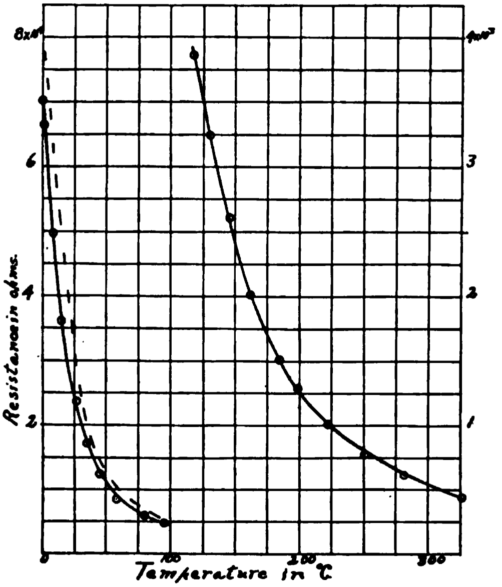

Fig. 4.

TABLE IV.

Temperature.	Resistance.	$S=1/R \cdot dR/dt$.	Δt
−3° C.	1 377		
−1.2	1,202		
0	1,116.01	.061	±.0033
.06	1,111.90		
.13	1,107.29		
.80	1,065.90		
1.1	1,049.61		
10	762.8		
11.2	745.9		
16.2	635.5		
19.51	570.81		
20.00	562.501	.030	±.0067
20.47	554.79		
20.81	549.21		
21.2	542.9		
22	520.5		
22.4	524.4		
23.1	514.3		
24.05	500.59		
25.00	487.92	.027	±.0074
26.12	473.58		
27.9	452.0		
28.9	440.0		
29.45	434.82		
30.00	428.94	.025	±.0080
30.33	425.42		

Temperature.	Resistance.	$S=1/R \cdot dR/dt$	Δt
44.1	295.7		
62.3	195.2		
90	125.5		
96.60	113.75		
97.13	112.81		
98.86	109.83		
99.82	108.21	.015	±.013
112.5	77.2		
120.6	67.8		
135.4	58.3		
155.4	50.0	.010	±.018 estimated from curve.
177.7	43.3		
201.5	37.6	.007	±.028 estimated from curve.
226.5	33.4		
245	30.5		
249	29.9	.0055	±.036 estimated from curve.
272	26.7		
302	23.5	.0047	±.042 estimated from curve.
340	20.3		
352	19.5	.0042	±.048 estimated from curve.
365	18.5		

In Table IV., S = sensibility of the thermometer No. 4 expressed in ohms change in resistance per degree centigrade per ohm. Δt = error involved in measuring a small change of temperature at the respective temperatures, assuming that the resistance can be measured with an error not greater than .01 of one per cent.

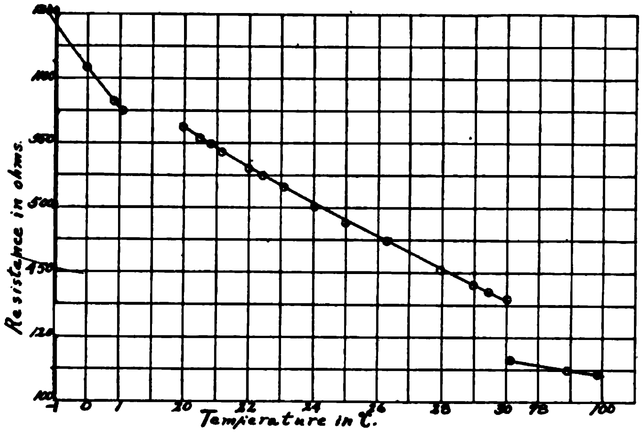

Fig. 5.

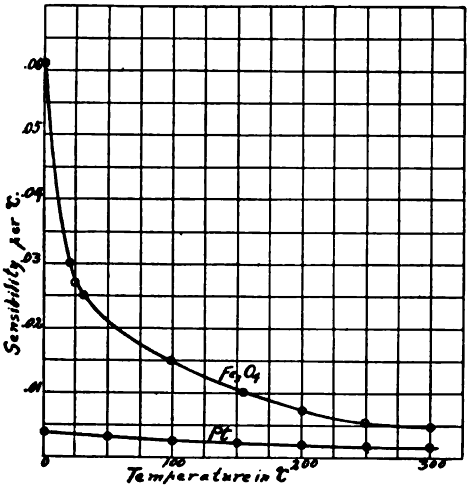

Fig. 6.

The temperature readings which are carried to the second decimal place were taken with a Beckmann thermometer.

Fig. 4 shows the variation of resistance of the magnetite with temperature.

Fig. 5 shows the resistance variation of thermometer No. 4 on an enlarged scale at room temperature, near zero, and near 100° C. The resistance of the magnetite between 10° C. and 30° C. can be expressed in terms of the resistance at 20° C. by

$$R_t = R_{20}(1.82 - .0524t + .00057t^2)$$

with an error of less than .2 of one per cent., where t is the temperature of the oxide in degrees centigrade. If the resistance of an iron oxide thermometer is accurately determined at a known temperature which is near 20° C., an unknown temperature which is greater than 10° C. and less than 30° C. can be determined by the aid of the above parabolic equation with an error of less than .1° C.

The sensibility of a magnetite thermometer and of the platinum resistance thermometer are shown graphically in Fig. 6. A comparison of the two curves shows that the magnetite thermometer is about 16 times as sensitive as the platinum thermometer at ice temperature, and about 8 times as sensitive at room temperatures.

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THE DIURNAL VARIATION OF THE EARTH'S PENETRATING RADIATION AT MANILA, PHILIPPINE ISLANDS.

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RUTHERFORD and Cooke[1] first called attention to the presence of a penetrating γ radiation, which they attributed to the presence of radio-active substances in the earth's surface. McLennan and Burton,[2] independently reported the discovery of a similar phenomenon. C. T. R. Wilson[3] had previously shown that the so-called "spontaneous ionization" of air in a closed vessel, which enabled it to conduct electricity, was also present when other gases were used; and that, further, the relative values of the ionization for these gases were approximately in the same ratio as those found for the same gases when acted upon by Becquerel rays. J. Paterson[4] called attention to the fact that the value of the ionization, when large vessels were used, was not proportional to the pressure, but tended towards a limit beyond which the ionization value was not increased by further increase of pressure. This pointed to the ionization being due to a feeble radio-activity of the walls of the vessel, the α rays from which were totally absorbed—under given conditions of size of vessel, of nature of gas, and of radio-activity of walls of vessel—for a given pressure. Since the relative values of the ionizations caused by α, β, and γ rays are, respectively, 10,000, 100, and 1, it is seen that the more easily absorbed α rays will practically determine the ionization in a vessel, the inside surface of which is radioactive. In order to test further this theory, Strutt,[5] used cylinders of the same dimensions but of different materials, and found the values for given pressures to vary with the material. Also, for different samples of the same material he found the ionization to vary. In the matter of reaching a maximum at a certain pressure, his results were in agreement with those of J. Paterson. Using one sample of tin-foil the maximum ionization was obtained at 29.8 inches pressure. For another sample of tin-foil the maximum was found at a pressure of 24.5 inches. This

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[1] Rutherford and Cooke, Amer. Phys. Soc., Dec., 1902.

[2] McLennan and Burton, Phys. Rev., 16, p. 184, 1903.

[3] C. T. R. Wilson, Proc. Roy. Soc., Vol. LXIX.

[4] J. Paterson, Proc. Camb. Phil. Soc., Vol. XII.

[5] R. J. Strutt, Nature, Vol. 67, p. 369, 1902.

investigator concluded that the ionization in a closed vessel was not spontaneous at all, but was due to the Becquerel rays from the walls of the ionizing vessel; and that radio-activity, instead of being rare, was everywhere present. It should be noted, in criticism of this conclusion, that the finding of different values for the radio-activity of different samples of the same material points to the activity being due to the presence of some of the rare radio-active substances as impurities in the metals of which the walls of the ionizing vessels were made, rather than to it being due to an inherent property of these metals. In order to reach some basis of comparison a crystal of uranium nitrate, having an exposed area equal to 48 sq. cm. was cemented inside of the cylinders. The rate of leak was then found to be thirteen times as great as when the most active sample of platinum was used for the ionizing chamber. The area of platinum exposed was 240 times that of the crystal. Therefore we may conclude that the uranium nitrate was about 3,000 times as active as the sample of platinum. Radium is about 100,000 times as active as uranium nitrate. So, the conclusion is reached that one part of radium to 300,000,000 parts of platinum would be sufficient to account for the observed activity. Prof. Armstrong,[1] in criticising this attempt to explain the nature of the ionization as being due to a radio-activity of the walls of the chambers, suggests that it might be due to some chemical change, such as oxidation. In answer, Strutt[2] makes the following clear-cut and concise statement, which undoubtedly furnished a basis for much of the later work on this very important subject:

"Prof. Armstrong suggests that the effect observed by myself and McClennan may be due to chemical change or to oxidation at the surface instead of to radio-activity. In speaking of the radio-activity of various metals, I mean that they exhibit effects differing only in degree from those shown by uranium and radium. These effects, observed experimentally, are as follows: (1) There is a leakage of electricity from a charged body in their neighborhood, the value of the leak being proportional to the E.M.F. for small E.M.F.s, and independent of it for large ones. (2) The effect varies with the pressure of the air in the chamber; being proportional to the pressure for small pressures; and, for large ones, independent of it, when E.M.F. is sufficient. (3) The rate of leak for positive electricity is the same as that for negative electricity. (4) The rate of leak does not depend upon the temperature. (5) When other gases are substituted for air the rate of leak is nearly proportional to the density of the gas, excepting for hydrogen, which

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[1] Prof. Armstrong, Nature, Vol. 67, p. 414, 1903.

[2] R. J. Strutt, Nature, Vol. 67, p. 439, 1903.

gives about one eighth the effect that air does. Every one of these points gives exact agreement between uranium and ordinary materials. On the other hand, I am not aware that any differences have been brought to light, except in magnitude of effect. Until such a difference should appear I think we may fairly and without dogmatism apply the maxim that similar effects are due to similar causes. In other words, we may conclude that the other substances, like uranium, are radio-active."

It was at about this time that Rutherford and Cooke, as previously mentioned, called attention to the result of experiments from which they concluded that a part, at least, of the ionization caused in a closed chamber was due to a penetrating radiation having its origin outside the chamber. They were able to reduce the ionization 30 per cent. by surrounding the chamber with lead sheets 3 cm. thick. A pig casting of lead, weighing 5 tons, and very much thicker than 3 cm., did not reduce the ionization any further. Surrounding the chamber with a considerable thickness of water reduced the ionization. Surrounding the instrument with wood or with brick increased the ionization, showing that these substances were radio-active or that a secondary activity was excited at their surfaces. Metals exposed outside the building for some time showed a marked increase in radio-activity over that which such metals had after having been carefully cleaned.

McLennan and Burton,[1] at about the same time reached the conclusion that, since they had been able to reduce the ionization in a closed vessel by 37 per cent., any explanation as to the cause of the ionization must take into account this penetrating radiation here shown to exist.

N. R. Campbell,[2] from a long series of observations which are very prettily analyzed, reaches the following conclusions:

(1) The influence which the walls of a containing vessel are known to exert upon the spontaneous ionization of the enclosed air, may be attributed to radiations proceeding from the walls. (2) That part of the radiation emanating from such substances as tin, zinc, graphite, and platinum is analogous to the secondary radiations excited by Röntgen and other such rays, being caused by the penetrating radiation which Cooke cut off with thick lead screens. (3) The coefficient of absorption of air for this radiation is comparable with that of air for α rays from radium. (4) The coefficient of absorption is different for different materials; and, therefore, it is improbable that the radiation is due to radio-active impurities. It is more probably due to an inherent property

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[1] McLennan and Burton, Phil. Mag., p. 699, Vol. 5, 1903.

[2] Norman R. Campbell, Phil. Mag., p. 531, Vol. 9, Ser. 6, 1905.

of the material. (5) That there is no evidence of the existence of rays, from ordinary materials, more penetrating than the α rays from radio-active elements. Finally, it is obviously of great importance to determine the nature of the rays from ordinary materials, their charge, their velocity, etc. The problem, however, will tax the ingenuity of the ablest experimenters.

This same line of investigation was continued by Alexander Wood.[1] He concluded that the ionization in a closed vessel was due, 1st to a penetrating radiation; 2d, to a secondary radiation caused by the penetrating radiation; and, 3d, to an intrinsic radiation from the walls of the vessel that is independent of the penetrating radiation. Some further results which he obtained are not pertinent to the matter in hand and so will not be considered here.

In a paper in 1905, A. S. Eve[2] concluded: (1) That the radium required to maintain a steady supply of emanation to the amount found per cubic kilometer of air near the earth is between 0.14 and 0.49 gm. (2) This amount of emanation and its successive products is sufficient to cause ions to be produced at the rate of 9.6 per c.c. per second. (3) The radium emanation in the air is probably sufficient to account wholly for the natural ionization in large closed vessels of non-radio-active materials, and for the rate of production of ions near the earth. However, in a paper in 1908, Eve[2] concludes, among other things, that the value of 4.5 ions per c.c. per second in a closed brass vessel as found by H. L. Cooke[3] cannot be attributed to the active matter in the atmosphere but that the radium present in the earth's crust is about of the right order of magnitude to account for it.

Wood and Campbell[4] concluded that there was a double diurnal variation in the ionization in a closed vessel, which appeared to be connected with the potential gradient changes in the atmosphere.

Wright, in Toronto, did not find such a diurnal variation.

G. A. Cline,[6] from a rather extended series of observations at Toronto, failed to detect a diurnal variation. He found that the penetrating radiation was greater after a fall of the barometer and smaller after a rise; the radiation was smaller when the ground was frozen and covered with snow than when it was bare and the temperature above freezing. The foregoing was for an open chamber. With a closed one he also

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[1] Alexander Wood, Phil. Mag., p. 550, Vol. 9, Ser. 6, 1905.

[2] A. S. Eve, Phil. Mag., p. 98, Vol. 10, Ser. 6, 1905.

[3] A. S. Eve, Phil. Mag., p. 189, Vol. 12, 1908.

[4] H. L. Cooke, Phil. Mag., p. 403, Vol. 6, Ser. 6, 1903.

[5] Wood and Campbell, Phil. Mag., p. 265, Vol. 13, 1907.

[6] G. A. Cline, PHYS. REV., p. 35, Vol. 30, 1910.

failed to find any regular diurnal variation, although there was a larger variation in the values at different times than when the open chamber was used. Different metals used for the chamber showed different activities; that for zinc being very low. The general conclusion was reached that the soil furnished by far the greater portion of the penetrating radiation present at the earth's surface at Toronto; and by comparison any that may have its source in the atmosphere or in the sun may be considered negligible in amount.

Ideal Method of Attacking Problem.—It has been pointed out a number of times that to be able to draw conclusions regarding the ultimate cause or causes of the radio-activity on the earth, it is necessary that a number of closely related phenomena be investigated at the same place, at about the same time, and by investigators working under the direction of one person. That the time and place should be the same is made necessary by the effect of geographical position, of climatic conditions, and of altitude upon the various radio-active constants the determination of which is to throw light upon the larger question of the radioactivity on the earth. The investigation should be conducted under one head so that it can be uniform and comparable; otherwise it is impossible to draw reliable conclusions from the rather disconnected data obtained. In short, there should be a cohesiveness, rather than an adhesiveness to hold together the various parts and make it one problem. There are four main heads under which the parts of this problem have been classified: (1) The determination of the radium content of the atmosphere. (2) The investigation of the nature and amount of active deposit on a negatively charged wire. (3) The qualitative and quantitative investigation of the penetrating radiation at the earth's surface. This investigation will give the necessary data to show whether there is a diurnal variation for the locality investigated. And (4) The determination of the value of the ionization of the atmosphere. There are two other closely related subjects that should be studied in connection with this problem. They may be classified as branches of the fourth main head above mentioned. They are: Potential gradient in the atmosphere, and nucleation of the ions in the atmosphere. It was under the inspiration of such an ideal scheme that Dr. J. R. Wright, professor of physics in the University of the Philippines, Manila, P. I., who was investigating the first of these four problems, started three members of his department on the three remaining problems. Due to the slowness with which it is possible to obtain apparatus at Manila, it was found necessary to deviate from the program. The result is that the first problem was thoroughly investigated, the report appearing in a paper by J. R. Wright and O. F. Smith.[1] The second problem was investigated by Mr. Blackwood, but no report of it has appeared to date. It was the intention of Wright and Smith to investigate the fourth problem. This paper is the report of the work done on the third problem.

Description of Instrument Used.—The instrument with which this investigation was carried on was a Spindler and Hoyer, aluminium-leaf electroscope, which had an ionization chamber 7.8 cm. inner diameter and a volume of 1850 c.c. A rod one mm. in diameter was connected to the leaf system of the electroscope, and was in the center of the ionization chamber. The electrical capacity of the chamber plus that of the electroscope was 8.6 E.S. units. The leaf could be read to tenths of a division, with a probable error of + or − two tenths. Fig. 1 is a photograph of the instrument. The larger of the three cylinders was used, throughout the observations, as the ionizing chamber.

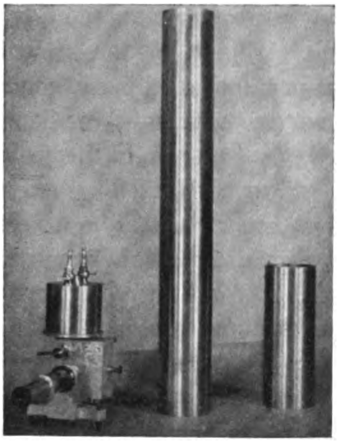

Fig. 1.

Procedure.—The procedure adopted was to seal off the ionization chamber, to connect one of the stop-cocks to an oil vacuum-pump, and the second to a drying tube and to a tube of cocoanut carbon, the two tubes being connected in series. The second stop-cock was closed and the chamber was exhausted to a vacuum of about two or three cm. Air was then slowly allowed to enter through the cocoanut carbon and drying tubes. In this way the chamber was filled with air that was dry and practically emanation free. Both stop-cocks were then closed and disconnected from everything outside. The chamber was not absolutely air-tight, but so long as the difference in pressure between the inside and the outside was small, there was very little tendency for air to leak out or in. The range of the one hundred scale divisions was from 346 down to 268 volts, assuring saturation voltages. To begin with the electroscope was simply charged and the deflection of the leaf for several hours observed.

Formula.—From the formula

$$N = \frac{C \cdot \Delta E}{V \cdot t \cdot e}, \qquad (1)$$

the value of N, which is the number of ions per c.c. per second formed in

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[1] Wright and Smith, The Philippine Journal of Science, Vol. 9, No. 1, Sec. A, Feb., 1914.

the chamber, was determined. The source of the radiation that caused the ionization in the chamber may have been in the earth's crust, in its atmosphere, or in some source external to the earth. Also, it may have been resident in the material of which the chamber was made, either as an inherent property of such material or as a result of contamination with some radio-active substance. Any leak over the insulation, which would have to be corrected for, if present, was guarded against by carefully cleaning the amber insulation with absolute alcohol and by drying the air that was allowed to enter the chamber. An open vial of concentrated sulphuric acid placed inside the electroscope proper kept the air therein dry.

It is evident that the charge necessary to cause the voltage of an insulated system, of capacity C, to drop by an amount ΔE, is given by

$$Q = C \cdot \Delta E. \tag{2}$$

Also, if N ions are formed per c.c. per second within the ionization chamber of volume V, for t seconds, and if each ion carries a charge of e E.S. units, then

$$Q = NVte. \tag{3}$$

Eliminating Q from (2) and (3), there results

$$N = \frac{C \cdot \Delta E}{V \cdot t \cdot e},$$

which is (1). The value of 4.77×10^{-10} E.S. units, as obtained by R. A. Millikan, was used for e. C and V were known, and t and ΔE are the variables that were observed.

Preliminary Results. It soon became evident that the value of N varied within wide limits, depending upon the time at which the observations were taken. This led to preliminary sets of readings, taken as follows: The electroscope was charged and allowed to stand about an hour before the first reading was taken. From this time on, for the next thirty-six hours, each scale reading and the time at which it occurred were recorded. The next twelve hours were taken up in resting. A period of about a week was spent in this way. Since the time of the scale readings did not fall on the hours or the half hours, it was necessary to interpolate to find what the readings were at each hour. Then, the change in scale reading per hour, reduced to E.S. units of P.D., gave the ΔE for one hour, *i. e.*, for $t = 3{,}600$ seconds. From (1) the value of N for each of the twenty-four hours of the day was calculated. This was done for each day and then the mean of N for each hour was obtained.

TABLE I.

Date.	12:00 M.	1:00 A. M.	2:00	3:00	4:00	5:00	6:00	7:00	8:00	9:00	10:00	11:00 A. M.	12:00 N.
5-18-13	....	....	....	....	....	....	....	....	....	....	....	....	....
5-19-13	1.14	1.28	1.14	1.07	1.06	1.07	1.13	0.80	0.73	0.73	0.71	0.72	0.99
5-20-13	....	....	....	1.03	1.14	1.21	0.91	0.69	1.01	0.51	0.62	1.62	1.00
5-21-13	1.52	1.21	1.13	1.15	1.13	1.17	1.02	0.86	0.87	0.55	0.57	0.59	0.65
5-22-13	....	....	....	....	....	....	....	....	....	....	1.40	1.41	0.83
5-23-13	0.81	1.58	1.22	1.13	1.13	1.17	0.99	0.94	0.65	0.73	0.81	0.82	0.90
5-24-13	....	....	....	....	....	....	....	....	....	....	....	....	1.50
5-25-13	1.26	0.87	1.49	1.14	1.44	1.22	1.23	1.13	0.61	0.46	0.79	0.91	0.83
5-26-13	....	....	....	....	....	....	....	....	....	0.62	0.63	1.23	1.24
5-27-13	0.91	1.00	1.06	1.24	1.03	0.96	1.05	0.97	1.22	0.93	0.66	0.70	1.37
5-28-13	....	....	....	....	....	....	....	....	....	0.57	0.66	0.89	...
5-29-13	1.39	1.08	1.01	1.08	1.13	1.18	1.29	0.68	0.93	0.72	0.59	1.09	0.49
5-30-13	....	....	....	....	....	....	....	....	....	....	....	....	....
5-31-13	1.05	1.35	1.40	1.28	1.25	1.22	1.01	0.85	0.84	0.51	0.42	0.71	1.02
6- 1-13	....	....	....	....	....	....	....	0.64	0.63	0.64	0.78	0.80	0.90
6- 2-13	1.10	1.03	1.11	1.30	1.28	1.36	1.24	0.81	0.72	0.77	0.92	0.87	0.83
6- 3-13	....	....	....	....	....	....	....	....	....	....	....	0.75	0.69
6- 4-13	1.35	1.24	1.14	1.02	1.17	1.11	1.21	0.68	0.68	0.69	0.66	0.75	0.80
6- 5-13	....	....	....	....	....	....	....	....	....	....	....	....	....
6- 6-13	1.39	1.25	1.24	1.00	0.94	0.95	1.13	0.96	1.15	0.89	0.62	0.50	0.74
6- 7-13	....	....	....	....	....	....	....	....	....	0.79	0.68	0.69	0.74
6- 8-13	1.00	1.18	1.27	1.10	1.15	1.06	1.30	0.87	0.76	....	....	0.65	0.72
6- 9-13	....	....	....	....	....	....	....	....	....	....	0.63	0.72	0.87
6-10-13	1.15	1.24	1.23	0.96	0.96	1.11	1.28	1.12	0.70	0.48	0.65	0.75	0.62
6-11-13	....	....	....	....	....	....	....	....	....	....	....	0.58	0.57
6-12-13	1.01	1.18	1.22	1.17	1.18	1.36	1.15	1.11	0.97	0.39	0.85	0.51	0.80
6-13-13	....	....	....	....	....	....	....	....	....	....	0.97	1.42	0.75
6-14-13	....	....	....	....	....	....	0.96	0.97	0.90	0.58	0.47	0.71	....
6-15-13	1.04	1.12	1.08	1.07	1.01	1.02	1.02	1.50	0.94	0.72	0.71	0.89	0.87
6-16-13	....	....	....	....	....	....	....	....	....	0.59	0.49	....	....
6-17-13	....	....	....	1.16	1.00	1.11	1.19	1.07	0.86	1.08	0.63	0.68	0.77
6-18-13	....	....	....	....	....	....	....	....	....	....	....	....	....
6-19-13	....	....	1.07	1.07	1.08	1.05	1.00	0.98	0.91	0.92	0.70	0.65	0.66
6-20-13	....	....	....	....	....	....	....	....	1.20	1.61	0.40	0.41	0.60
6-21-13	....	....	....	....	....	1.06	1.06	1.17	0.85	0.83	0.84	0.84	0.83
6-22-13	1.03	....	....	....	....	....	....	....	....	....	....	....	....
Mean divs. per hour........	1.143	1.186	1.187	1.116	1.122	1.134	1.114	0.940	0.862	0.720	0.700	0.829	0.843
Mean ions per c.c. per second......	8.06	8.35	8.36	7.87	7.92	8.00	7.85	7.63	6.08	5.08	4.94	5.81	5.95

Table I.

1:00 P. M.	2:00	3:00	4:00	5:00	6:00	7:00	8:00	9:00	10:00	11:00 P. M.	Average for the Day.	Weather Conditions.
....	....	....	....	....	....	....	1.43	1.19	0.83	1.29	1.19	Fair
1.11	0.69	1.07	1.37	1.20	1.22	1.23	1.40	1.00	....	....	1.04	"
0.82	1.16	1.56	1.15	0.93	1.12	1.14	1.29	1.31	1.01	0.76	1.05	"
0.75	1.12	1.14	1.03	1.04	1.03	1.55	1.07	....	....	....	1.01	"
0.92	1.11	1.31	1.06	1.62	2.22	1.39	1.12	1.04	1.32	1.28	1.29	"
1.29	1.12	0.92	1.13	1.07	0.96	1.13	1.32	....	....	....	1.04	"
1.25	0.49	0.63	1.00	1.54	1.65	1.63	0.66	1.38	1.46	1.39	1.22	"
0.95	1.88	0.66	1.04	0.94	1.32	1.61	....	....	....	....	1.09	"
0.78	1.26	1.98	1.60	0.93	0.93	1.24	1.32	0.99	0.83	1.19	1.12	Light Rain
1.27	1.19	1.15	0.96	0.98	1.13	1.20	1.20	....	....	....	1.06	" "
....	....	....	....	2.39	1.38	1.56	....	....	....	....	1.24	Fair
0.55	0.44	1.05	1.65	1.09	0.98	1.22	1.62	0.94	....	....	1.01	"
....	....	....	1.28	1.19	1.62	1.43	1.13	1.21	1.17	1.32	1.33	"
1.23	1.25	0.93	1.02	1.14	1.06	1.32	1.74	....	....	....	1.08	"
1.02	0.91	0.87	....	....	1.34	1.59	1.43	1.53	1.09	1.18	1.02	"
0.96	1.22	0.96	1.27	1.40	1.30	1.24	1.09	0.27	....	....	1.05	"
1.15	1.15	0.94	1.14	0.96	1.05	1.48	1.44	1.26	1.11	1.04	1.09	"
0.79	1.14	1.37	2.26	1.25	0.74	....	....	....	....	....	1.05	"
....	....	....	....	....	....	1.25	1.28	1.24	1.17	1.26	1.24	Heavy rain
0.74	0.58	1.21	1.97	0.63	0.98	1.21	1.01	....	....	....	1.00	Fair
0.79	1.01	1.01	1.26	....	....	....	....	1.03	1.20	1.01	0.93	"
0.86	0.81	1.03	1.33	1.12	0.88	1.26	1.12	0.85	....	....	1.08	"
0.74	0.97	1.56	1.38	1.24	1.09	1.06	1.17	1.08	1.06	1.03	1.04	"
0.86	1.42	....	....	....	1.42	1.22	....	....	....	....	1.01	Rain
0.57	1.02	0.93	1.06	1.08	0.86	1.13	1.36	1.18	1.21	1.18	0.98	Fair
0.74	0.78	1.05	1.60	0.35	1.48	0.86	1.31	1.67	....	....	1.04	Heavy rain
0.88	0.93	1.30	1.32	....	....	....	....	1.03	1.05	....	1.07	Fair
....	0.85	0.89	1.40	1.36	1.39	1.05	1.08	1.17	1.18	1.18	1.01	"
0.79	0.84	1.02	1.20	1.12	1.05	1.11	0.99	....	....	....	1.01	"
....	....	1.23	1.02	1.29	1.21	1.71	1.33	....	....	....	1.11	"
0.77	1.09	0.99	1.28	1.19	1.01	0.92	1.03	....	....	....	0.99	Heavy rain
....	0.73	1.02	1.33	1.26	1.07	1.02	1.08	....	....	....	1.07	" "
0.79	1.08	1.16	....	....	1.10	1.43	1.11	0.97	1.06	....	0.99	" "
0.72	0.77	1.26	1.21	1.13	1.16	1.00	0.98	1.45	1.22	0.94	1.01	Fair
0.75	0.97	1.03	0.97	1.21	1.06	1.02	1.23	....	....	....	0.99	"
....	1.34	1.10	0.88	0.90	0.94	0.86	0.86	0.98	....	....	0.99	"
0.884	0.976	1.111	1.272	1.158	1.180	1.252	1.208	1.129	1.123	1.146	1.055	
6.26	6.88	7.81	8.96	8.15	8.31	8.82	8.50	7.95	7.90	8.06	7.43	

These *N*'s were plotted against times as shown in Fig. 2. While the curve is rather irregular, there certainly is a decided minimum at 11 A. M. and a decided maximum at 4 P. M. The mean *N* for the minimum at 11 A. M. is 5.2, and that for the maximum at 4 P. M. is 11.5. The maximum is, therefore, more than twice the minimum. The mean is practically the same whether it be obtained by averaging all the 24 values for the different hours of the day, or by averaging only the maximum and the minimum. The former method gives 8.05 for mean *N*, and the latter gives 8.35.

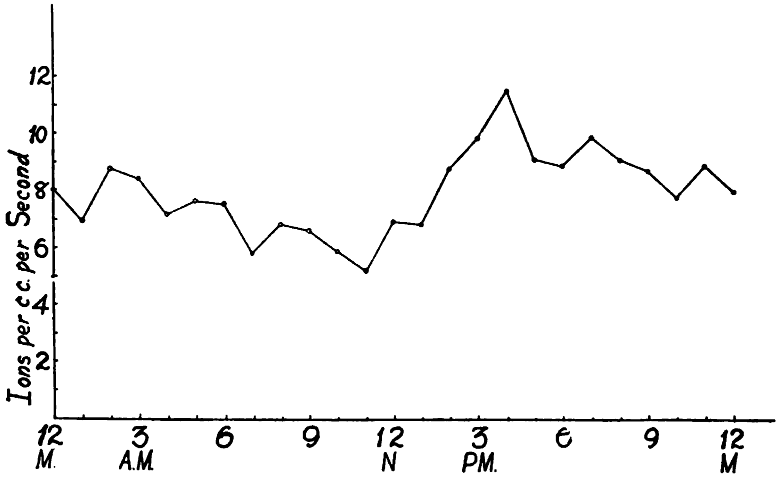

Fig. 2.

Final Results.—This preliminary test seemed conclusive in establishing the fact that there was a true diurnal variation in the value of the penetrating radiation at Manila. But it was felt that a longer series of observations was needed to determine more accurately the time of the maximum and of the minimum as well as their value and the value of the mean. With this object in view, the electroscope and ionization chamber were set up in a stone bungalow, the residence of the author, at 217 Valenzuela, Santa Mesa, Manila, P. I. This was considered a desirable location as it was far from any possible source of radio-active matter, such as might be present in the neighborhood of a physical or chemical laboratory. It was also at one of the highest spots in Manila, and the air had free access from all directions. Another important consideration, since readings extended over 36-hour periods, was that rest could be obtained between readings. Thanks are due to Mrs. L. J. Lassalle who frequently made the observations from five to ten A. M. Had it not been for this aid, it would not have been possible to observe 36 hours out of each 48, as was done.

Final Series Shows a Diurnal Variation.—Table I. is a complete record of the calculations for N obtained from the data taken during the period extending from May 18, 1913, to June 22, 1913. The calculations consisted of interpolations so as to get the scale readings at each half hour. Then, the difference between the readings for one mid-hour and the next gave the change in scale-readings per hour. It is evident that this difference is proportional to ΔE. Since C V, t, and e are constant for a given instrument, this difference is proportional to N, the number of ions per c.c. per second formed in the ionization chamber. In this case $N = 7.05 \times$ divisions per hour. In Fig. 3, N is plotted against time. The curve shows a decided minimum at 10 A. M. equal to 4.94 and a decided maximum at 4 P. M. equal to 8.96, the maximum being nearly twice the minimum. The mean obtained by averaging all 24 values is about 7 per cent. higher than that obtained by averaging the minimum and the maximum. The minimum N is practically 5 and the maximum is practically 9. *These observations seem to establish the fact beyond a doubt, that there is a true and decided diurnal variation in the value of the ionization in a closed vessel at Manila, P. I.* It would be very interesting to have observations of this nature extended over a whole year, so as to see whether or not the nature of the variation would change with changing seasons. These observations are for the end of the dry season, just before the beginning of the wet or typhoon season.

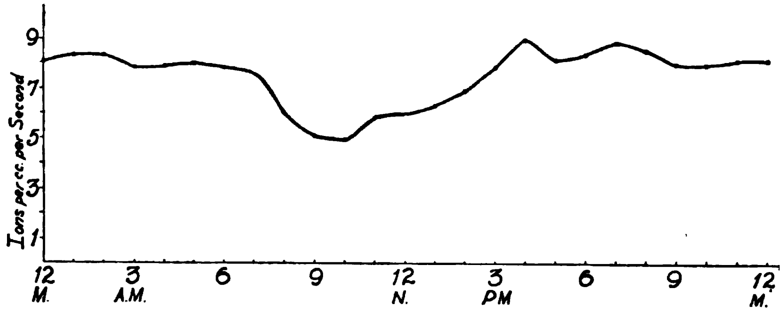

Fig. 3.

Further Deductions from the Data Obtained.—The results obtained do more than show a diurnal variation; they throw some light on the nature of the cause or causes of the ionization in a closed vessel. The possible causes are:

1. Radio-active gases in the vessel, but having their origin outside of it;
2. Radio-active impurities in the material constituting the vessel;
3. An inherent radio-activity of the material constituting the vessel;

4. A penetrating radiation from the radio-active matter known to be in the earth's crust;

5. A penetrating radiation from the radio-active matter known to be in the earth's atmosphere;

6. A penetrating radiation from the sun or other non-terrestrial sources. In addition, a leak over the insulation of the leaf system would cause a deflection of the leaf that would be supposed to be due to an ionization in the vessel. Therefore, we may classify as

7. A leak over the insulating system of the leaf.

The effect of (1) was practically eliminated by allowing the vessel to remain closed for about two weeks before the observations were taken. Radium emanation has a half-period value of 3.85 days; and in 15 days its activity will decay to about 7 per cent. of its original value. Also, the air allowed to flow into the tube, after it had been exhausted to a vacuum of about 3 or 4 cm., was passed over cocoanut carbon in a long tube, thus robbing it of almost all the emanation in the first place. Thorium emanation has a half-period value of 53 seconds, while for actinium emanation the value is 3.9 seconds. It is evident that even if some of these gases did enter at first, their activity would have decayed to practically nothing in two weeks.

It may be that either or both of 2 and 3 produce the ionization in the vessel. However, their effect in the present instance must have been small, for after sealing off the tube in the manner previously mentioned the mean value of N for each of several successive days was calculated. There was no indication of a gradual rise in the value of N, as would necessarily have been the case had there been any radio-active materials, either as impurities or otherwise, in contact with the air within the vessel. Also, there could hardly be any explanation of the diurnal variation in the value of the ionization having its origin in either 2 or 3. The only theory that it would be reasonable to advance would be that a temperature variation might cause the emanation from the inner walls of the vessel to be given off more rapidly when the temperature is high than when it is low. However, the temperature at Manila during fair weather is appreciably constant from 10 A. M, to 4 P. M.; and it is between these hours that N varies from its minimum to its maximum. It is therefore, reasonable to conclude that the effect of 2 and 3 is small in this particular vessel.

If radio-active matter in the sun furnished any appreciable cause of the ionization, one would expect the minimum to occur at night. However, there might be a lagging of the effect after the cause is removed. Even then it would be expected that the variation would give a more symmetrical curve than the one obtained. That is it would be reasonable to expect the period of highest value and that of lowest value to each extend over twelve hours, even though the former did not fall during the day and the latter during the night. The best evidence that the sun is not a factor is furnished by the work of Simpson[1] at Karasjoh in Norway, which shows that the active matter deposited on a negatively charged wire is about the same in amount in summer, as in winter when the sun does not rise above the horizon. Other non-terrestrial sources are so numerous that it would not be advisable to try to consider them here. Suffice it to say that it seems improbable that any other source, not on the earth, would be as likely to be the source of the ionization as would be the sun.

A leak over the insulation was guarded against by drying the air that entered the vessel and by freeing it from dust particles. It was also observed that, when the vessel was exhausted the leaf did not appreciably deflect for several hours. We may, therefore, say that the effect of 7 was very small.

Thus we have 4 and 5 left as the main causes of the ionization in the closed vessel. One cannot offer any explanation of a possible diurnal variation in the amount of radio-active matter in the soil in Manila. Since we assume the effect of all other causes excepting 4 and 5 to be small, and since the effect of 4 is assumed steady during the time over which these observations extend, the conclusion is forced upon us that the diurnal variation is a variation in the value of the penetrating radiation from the earth's atmosphere. Since N varies from 5 to 9, it is also evident that the effect of the active matter in the atmosphere is responsible at times for at least 4 ions per c.c. per second at Manila. The cause of the diurnal variation is probably that the air which sweeps over this locality at certain times has been over water for a long enough period of time to have lost some of its activity by decay. At other times the air comes from over the land, so that it is in radio-active equilibrium with the active matter in the earth's crust. That is, whatever activity it is gaining is equal to that which it is losing by decay. At a given season of the year there is a steady recurrence of sea and land breezes at Manila; so that it is to be expected that there will be a steady recurrence of the maximum and of the minimum for the ionization in a vessel if this ionization is due at all to the active matter in the atmosphere. In addition to the shifting of the air from land to sea and vice versa, due to temperature changes, there is generally another motion of the air, called a typhoon. There may also be vertical air currents. Since the

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[1] Simpson, Phil. Trans. Roy. Soc., *A*, 205, p. 61, 1905.

data to determine these three components is not at hand it is impossible to determine exactly the direction of the resultant at any time. While it would be rather difficult to determine these factors, they are necessary to a complete solution of the problem in hand. It is not to be expected that such a variation will be found at points where there are no considerable bodies of water near, over which the air might remain long enough to lose a considerable part of its activity.

It was thought possible that the value of *N* might be connected with the kind of weather which prevailed while the observations were being taken. Most of the five weeks were fair, but there was one period at the beginning of the fifth week when there were heavy rains for three days. There were two or three other days when there were heavy rains. The mean of *N* for all periods following heavy rains is 7.16 while the mean for the remaining time is 7.72. It is to be expected that following heavy rains the pores of the earth will be filled so that the radio-active gases will not be able to escape so readily. However, the data at hand from which to draw conclusions regarding this matter is rather limited as the difference is very small for clear and for rainy weather. The time to get data on this point is during the rainy season.

SUMMARY.

1. A diurnal variation in the value of *N*, the number of ions per c.c. per second formed in a closed vessel in Manila, was found, The maximum of 8.96 occurs at 4 P. M., and the minimum of 4.94, at 10 A. M. The mean for *N* is found to be 7.43.

2. It seems probable that the main causes of the ionization are the radio-active materials in the soil and the radio-active matter in the atmosphere.

3. Since there is no reason to suppose that the former of these two causes might have a diurnal variation, it must be that this variation is in the latter cause.

4. The air currents at Manila have a diurnal variation, sea breezes blowing at times and land breezes at other times. While the exact nature of the relationship cannot be established from the data available, it seems probable that the minimum must occur at a time when the air over the land is air that has blown from over the sea where it has previously remained long enough to lose a considerable portion of its activity by decay. The maximum, which is fairly steady from 3 P. M. to 6 A. M., must be due to the air which is over land during this period having previously been mainly over land for some considerable time.

STATE COLLEGE, PA.

AN ADDITION TO A THEORY OF IONIZATION BY IMPACT.

By H. W. Farwell.

SOME time ago Bergen Davis[1] developed a theory of ionization by impact which has been very suggestive and of particular interest in the consideration of non-elastic impacts. The experiments of Franck and Hertz[2] have shown that in certain gases, such as oxygen, nitrogen, and hydrogen, the impacts are practically all of this character, so that this assumption in Davis's theory is not without support in experiment. The lack of accord between this theory and some of the experimental evidence is due to the fact that the impacts in all cases were originally considered to be non-elastic. In confining attention now to those gases in which the impacts have been shown to be of this kind, there is still cause for differences between fact and theory.

The original paper assumed that there were present in the space ionized all possible ionic paths between zero and infinity, whereas of necessity many of the experiments have been carried out with relatively small distances between the plates of the condenser. It is hardly necessary to point out that under such conditions the average number of ionizing impacts per centimeter can not be determined with accuracy, and differences between theory and results of such experiments may be held against the experiment rather than against the theory.

It seemed worth while to extend the theory to cover all such cases, though the method of calculating the number of ionizing impacts may still cause small differences. Following Davis's reasoning exactly the number of ionizing impacts which an ion makes in traversing a distance dx just beyond a path $\lambda_0 + x$, where λ_0 is the shortest path along which the necessary energy for ionization can be acquired, is given by

$$\frac{1}{l}\epsilon^{-\frac{\lambda_0+x}{l}}\frac{x}{\lambda_0+x}\frac{dx}{l},$$

where l is the mean free path of the ion. If now the ion is in a field due to a condenser whose plates are a distance D apart, the quantity x may have any values between 0 and $D - \lambda_0$. The complete expression

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[1] Phys. Rev., XXIV., p. 93, Jan., 1907. Also Ann. d. Phys., 42, p. 807, 1913.

[2] Ber. d. Deuts. Phy. Ges., 15, p. 613, 1913. Also p. 929, 1913.

for the number of ionizing impacts per centimeter is then

$$\alpha = \frac{1}{l}\int_0^{D-\lambda_0} \epsilon^{-\frac{\lambda_0+x}{l}} \frac{x}{\lambda_0 + x}\frac{dx}{l}.$$

This expression is, like the original, not integrable in finite terms, but can be integrated in a form involving the exponential integral.[1]

The solution is

$$\alpha = \frac{1}{l}\left\{\left[\epsilon^{-\frac{\lambda_0}{l}} + \frac{\lambda_0}{l}Ei\left(-\frac{\lambda_0}{l}\right)\right] - \left[\epsilon^{-\frac{D}{l}} + \frac{\lambda_0}{l}Ei\left(-\frac{D}{l}\right)\right]\right\}$$

where *Ei* ( ) denotes the exponential integral. This is Davis's solution with a correction term added, and reduces to his solution when the distance between the plates is large.

The magnitude of the correction term can be computed for any given conditions, but to avoid tedious calculation the curves below have been plotted to represent the amount of this correction under various conditions. The abscissæ give the ratio of plate-distance to ionic mean free path, and the ordinates give the magnitude of the quantity $\epsilon^{-\frac{D}{l}} + (\lambda_0/l)$ $Ei(-D/l)$ expressed in per cent. of the quantity αl, or in other words the ordinates give the per cent. error in determining α for a given pressure. The curves have been plotted only for the range of values likely to occur

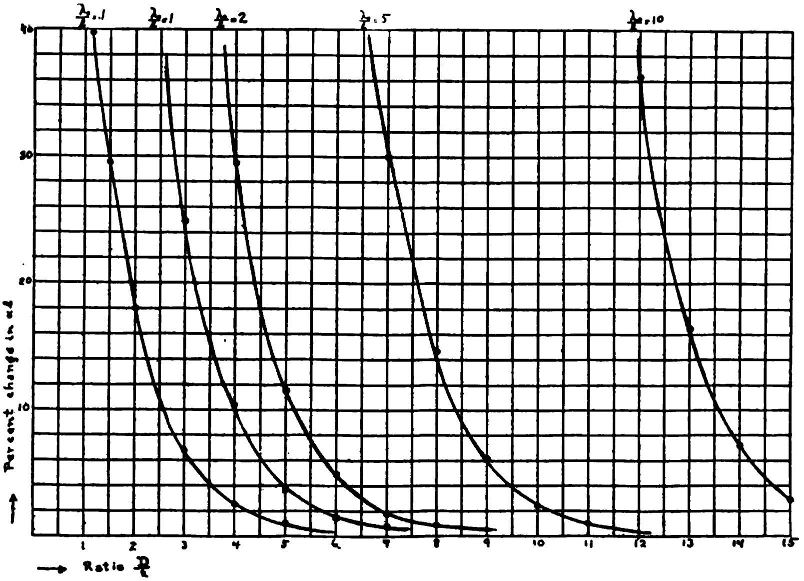

Fig. 1.

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[1] Bierens de Haan, Verh. Kon. Ak. Wet., Vol. II., 1854, p. 214.

in observations of the current between parallel plates, and give at once the error if the observer has a measure of D and l. Curves of this sort may be used to determine the lower limit for plate distance in experimental work. Without mentioning the specific instances it may be remarked that there are numerous cases where experimenters have taken observations with plates separated by such a small distance as to lead to errors in α of fairly large magnitude.

Partzsch[1] has made a similar addition to Townsend's expression for the current

$$n = n_0 \epsilon^{\alpha D}$$

since this expression would indicate an increase in the current even though the applied voltage was less than the ionizing voltage. Expressed in symbols already used, Partzsch's modification may be written

$$n = n_0 \epsilon^{\alpha D\left(1-\frac{\lambda_0}{D}\right)} = n_0 \epsilon^{\alpha(D-\lambda_0)}.$$

This, like Townsend's, gives from the experimental results the values of α, but the reasoning from it to deduce the ionizing voltage would be open to the same objections as those made by Franck and Hertz[2] to the original form.

This addition to Davis's formula is in itself of minor importance, but it may serve to aid further inquiry into the process of ionization by impact and the character of electron paths.

Phœnix Physical Laboratory,
Columbia University,
October 15, 1914.

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[1] Verh. Deutsch. Phys. Gesell., 14, p. 60, 1912.

[2] Ber. Deutsch. Phys. Gesell., Jan. 15, 1914.

ATOMIC NUMBERS AND ATOMIC CHARGES.

BY FERNANDO SANFORD.

IN a paper entitled "Untersuchungen ueber das System der Grundstoffe" (Lund, 1913), Rydberg has undertaken to show that the properties of the elements which determine their positions in the periodic series may be calculated from the number which represents the order of their occurrence in this series. Thus he says:[1]

"In the system of Mendelejeff all the elements are arranged in a single series, and each element is distinguished from all others by its place in this series. This signifies that *a single independent variable suffices to completely determine each element.* According as a quantity to be determined varies continuously or discontinuously must the independent variable pass through the continuously increasing series of all numbers or the discontinuous series of the positive whole numbers. In the case before us one cannot doubt that the properties of the elements vary discontinuously from element to element. Continuous variation in the properties of the elements may, indeed, occur, but only in consequence of a continuous change in temperature, pressure, and the like, of the same element. Between the individual elements there is no continuous transition.

"We are accordingly led to the adoption of the series of the positive whole numbers as the independent variable for the system of the atoms."

Rydberg then undertakes to show that the characteristics of the atoms upon which the periodic law was based may be calculated by means of the mathematical relations between their atomic numbers. He does not propose any physical explanation of these numerical relations.

Such a physical relation is suggested in a discussion by A. van den Broek, entitled Die Radioelemente, das periodische System und die Konstitution der Atome.[2] van den Broek concludes from the change in atomic weight of the elements produced by radioactive changes that, in general, the atomic weight changes from atom to atom in the periodic series by about two units, and that the deviations from this law are accidental.[3] He also assumes that each change in atomic weight is

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[1] Translation by present writer.

[2] Phys. Zeitsch., XIV., 32 (1913).

[3] See article by present writer in Jour. Am. Chem. Soc., XXXIII., 1349 (August, 1911) and Theo. Wulf, Phys. Zeitsch., XII., 497 (1911).

accompanied by the gain or loss of a definite electrical charge, hence the positive sub-atom or nucleus of an elementary atom should carry a charge proportional to the serial number of the atom in the chemical series. This hypothesis gives a physical significance to the atomic numbers which Rydberg regards as the descriptive characteristics of the elements.

Previous to this Rutherford[1] and Barkla[2] had concluded from the scattering of α-particles and of X-rays that the elementary atom carries a positive charge which is proportional to half its atomic weight. van den Broek concludes that the atomic number should be substituted for half the atomic weight in the above hypothesis.

In the recent work which has been done upon the spectra of the X-rays given off by various elements when these are bombarded by cathode rays it has been found that in its high frequency radiation as in its visible radiation each element has a characteristic spectrum. The work of the Braggs, of Mosely and Darwin and, more recently, of Mosely has shown that the X-ray spectra of the different elements are very similar; that they are, in general, characterized by five lines of much greater intensity than the rest of the spectrum, and that corresponding lines in the spectra of different elements may be identified. When the relative frequencies of these lines are determined by reflection from the same analyzing crystal, it has been found that this vibration frequency is greater the higher the atomic weight of the element.

In his paper in Phil. Mag., XXVII., 703 (1914), Mosely has extended his measurements on X-ray frequencies to include all the elements from aluminium to gold, and has related the frequencies of corresponding lines in different spectra to the serial numbers of the respective atoms in Mendelejeff's table. He concludes that the vibration frequency of the line α (α being the line of lowest frequency in the X-ray line spectra of the elements) varies as the quantity $(N - k)^2$, where k is a constant and N is the serial number of the element, aluminium being taken as 13.

Mosely then concludes from a discussion of Rutherford's theory of atomic structure that the change in frequency of the vibrating electrons which produce this line must be due to a change in the magnitude of the positive charge on the nucleus of the atom. He states his conclusions as follows:

1. Every element from aluminium to gold is characterized by an integer N which determines its X-ray spectrum. Every detail in the spectrum of an element can therefore be predicted from the spectra of its neighbors.

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[1] Phil. Mag., XXI., 669 (1911).

[2] Ibid., XXI., 648 (1911).

2. This integer N, the atomic number of the element, is identified with the number of positive units of electricity contained in the atomic nucleus.

3. The atomic numbers for all the elements from Al to Au have been tabulated on the assumption that N for Al is 13.

4. The order of the atomic numbers is the same as that of the atomic weights, except where the latter disagrees with the order of the chemical properties.

5. Known elements correspond with all the numbers between 13 and 79 except three. There are here three possible elements still undiscovered.

6. The frequency of any line in the X-ray spectrum is approximately proportional to $A(N - b)^2$, where A and b are constants.

Mosely does not give a table of frequencies of the same line for all the elements he has examined, but on page 709 of his paper he gives curves showing both the wave-length and the square root of the frequency of many of these lines plotted against the atomic numbers. These curves are very approximately straight lines. It accordingly seems that whether the charge of the positive nucleus of an atom is, or is not, proportional to the atomic number, N, the frequencies of the principal lines of the X-ray spectra are proportional to the squares of these atomic numbers.

The present writer has published several papers in this journal and in others, beginning in 1911,[1] in which it has been shown that the product of the atomic weight of an element multiplied by the migration velocity of its ion in the electrolysis of dilute water solutions gives a number which has been shown to be related to all the properties of elements and their compounds which depend upon affinity or cohesion, as well as to many optical properties and to the dielectric constants of several of the elements. It may accordingly be worth while to compare the atomic constants calculated in this way with the atomic charges which van den Broek and Mosely infer from the atomic numbers.

Since the ionic mobilities given by different investigators differ by considerable quantities, I have used in this comparison only the elements and the ionic velocities given in Kaye and Laby's Tables. Mobilities are there given for twenty elements. These elements with their atomic numbers as given by Rydberg,[2] and their atomic charges as calculated by me, assuming the charge on the hydrogen ion as 5, are given in the table below.

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[1] PHYS. REV., XXXII., 512 and 518; XXXV., 276; N. S., I., 211 and 446. Astrophys. Jour., XXXV., 1; XXXVI., 255.

[2] Since Rydberg introduces two hypothetical numbers between hydrogen and helium, Mosely's atomic numbers are each two less than the number for the same atom as given by Rydberg. This will make no difference in the curves plotted for the present article.

TABLE I.

Element.	*N*	Chg.	Element.	*N*	Chg.
H.	1	5	Br.	37	84.9
Li.	5	3.6	Rb.	39	91.2
F.	11	14.6	Sr.	40	71.5
Na.	13	15.7	Ag.	49	91.6
Mg.	14	17.3	Cd.	50	83.8
Cl.	19	36.5	I.	55	132.5
K.	21	39.6	Cs.	57	142
Ca.	22	32.5	Ba.	58	119.4
Cu.	31	46.7	Tl.	83	212
Zn.	32	47.6	Pb.	84	199.4

It will be seen from the above table that while the atomic charges increase as the atomic numbers increase they do not increase at the same rate for the univalent and divalent ions. This has been shown elsewhere for all the other properties which seem to depend upon the atomic charges. The relation of these two sets of charges to the atomic numbers are shown graphically by the two curves in Fig. 1.

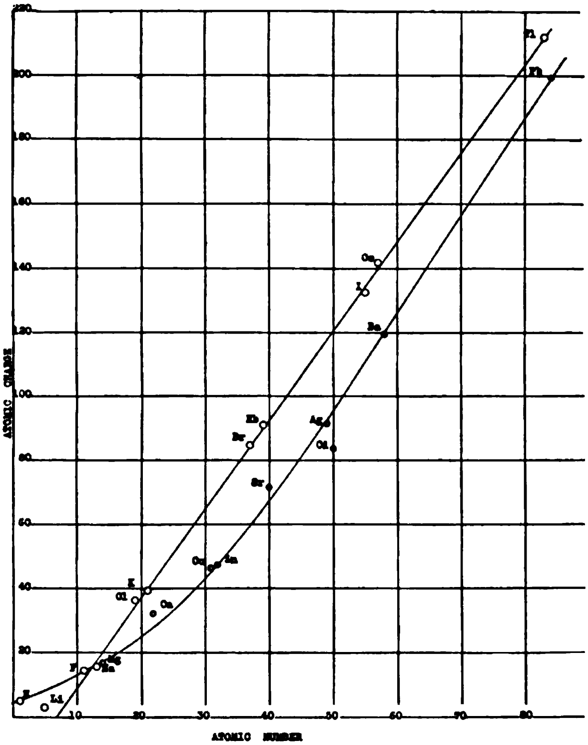

Fig. 1.

It will be seen from these curves that a straight line relation exists between the atomic charges of the univalent ions and their corresponding atomic numbers, and hence that these charges may be accurately calculated from the atomic numbers. This does not seem to be so generally true of the divalent elements, though these, with the exception of cadmium, lie on a smooth curve which does not differ much from a straight line for the elements heavier than calcium. The case of cadmium does not necessarily furnish an exception, since it is known that cadmium salts are usually made up of complex molecules which ionize by successive steps, so that in solutions of finite concentration both ions usually contain cadmium. This makes the determination of the transference number for cadmium very difficult, if not impossible, and would regularly make it appear too low, as is indicated by its atomic charge.

Since the frequencies of corresponding lines in the X-ray spectra of the elements may be calculated from the atomic numbers, it follows that for the monovalent elements, at least, they may be calculated from the atomic charges determined in electrolysis.[1] It does not necessarily follow, however, that the charges of the ions determined in electrolysis are the same as the charges of the positive atomic nuclei in the Rutherford atom. In fact, they cannot be the same, since the charges calculated for the halogen ions in electrolysis are electronegative.

The distinction between the properties of the electropositive and electronegative atoms has been shown in many ways by the present writer, though it is now seen that the magnitude of both kinds of charges may be calculated from the atomic numbers. Thus, while all the properties depending upon cohesion have been shown to be quantitatively related to the atomic charges, the magnitude of cohesion increases with the increase of the negative atomic charge but decreases with the increase of the positive atomic charge. This relation, which has been shown in previous papers, may also be exhibited by plotting the magnitude of such properties as compressibility, melting point, boiling point, critical temperature, hardness, and the like, against the atomic numbers of the elements. Thus, Fig. 2 shows graphically the relation of the melting points of the alkali metals and of the electronegative halogen elements to their respective atomic numbers. I have previously shown that the melting points of the alkali metals may be calculated

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[1] In this connection it may be mentioned that in Astrophysical Journal, XXXVI., 255 (Oct., 1912), the present writer has shown that the convergence frequencies in the spectral series of a number of elements may be calculated from their atomic charges. It follows that these may also be calculated from the atomic numbers, and that the frequencies of the visible spectra as well as the X-ray spectra may be shown to be related through the atomic numbers or atomic charges.

from their atomic charges as accurately as they can be measured. They may also be calculated to a high degree of approximation from the equation $(N + 3)(T - 275) = 1{,}497$, where N is Rydberg's atomic number and T is the melting point, absolute.

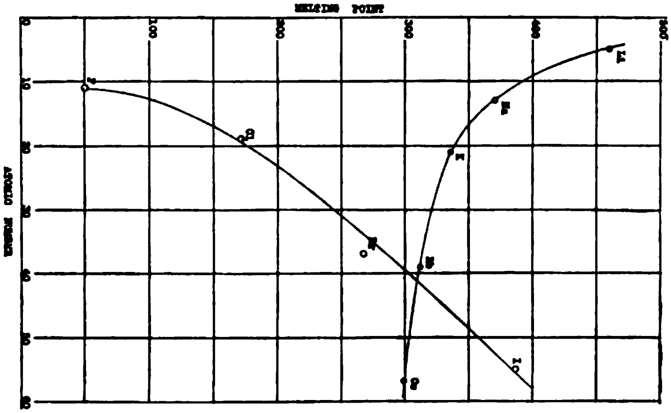

Fig. 2.

A similar relation between atomic numbers and melting points may be shown for many closely related groups of elements, but while within a given group the melting point is higher the more electronegative the

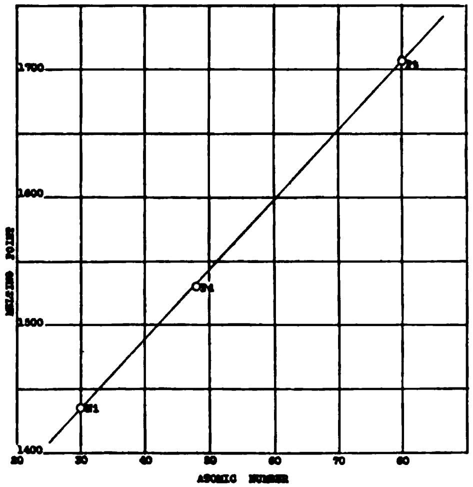

Fig. 3.

element, the melting point may either increase or decrease with the atomic number, as is shown in Fig. 2. Examples of the increase of melting point with the increase of the atomic number in metals may be shown in the three similar groups, iron, ruthenium, osmium; nickel, palladium, platinum; cobalt, rhodium, irridium. This relation for nickel, palladium and platinum is shown graphically in Fig. 3. The melting points used are those given in Kaye and Laby's Tables. Within each set of triplets from which the above elements are taken, on the contrary, the melting point decreases as the atomic number increases.

The above considerations make it seem to the writer that while the electrical properties of the elementary atoms are in some manner closely related to their respective serial numbers, it is not probable that these numbers represent in all cases the magnitudes of the electropositive charges of the sub-atoms.

STANFORD UNIVERSITY,
October 3, 1914.

TEMPERATURE CHANGES ACCOMPANYING THE ADIABATIC COMPRESSION OF STEEL.

By K. T. Compton and D. B. Webster.

Introduction.

THE formulæ of Clapeyron, which apply to reversible transformations of a body whose state is a function of two independent variables, lead to the conclusion that all substances which expand when heated will experience a rise in temperature when mechanically compressed, and vice versa. It was first shown by Lord Kelvin[1] that, as a result of the second law of thermodynamics, the rise in temperature $\Delta\theta$ produced in a rod or wire by an increase ΔF in the stretching force should be expressed by the equation

$$\Delta\theta = -\frac{a\theta}{\pi r^2 \rho s J}\Delta F,$$

where r and ρ are the radius and density, respectively, of the wire, a is its thermal coefficient of expansion, s is its specific heat, θ is the absolute temperature and J is the mechanical equivalent of heat.

Joule[2] first attempted a verification of this equation by measuring the temperature changes produced by suddenly stretching or compressing various liquids, metals, wood, rubber, etc. Although in a general way Joule's observations agree with the theory, there is an average discrepancy between theory and experiment amounting to about 15 per cent.

Later Edlund,[3] experimenting with metal wires, showed that the *relative* temperature changes in different metals may be accurately predicted by Thomson's formula, but failed to prove the *absolute* accuracy of the formula. In the case of steel, for instance, the apparent temperature increase was only 63 per cent. of that predicted by the formula.

By using a greatly improved method of measuring small temperature changes in wires and by taking into account the effect of possible variations in the thermal coefficient of expansion of the wire at different tensions,[4] Haga[5] succeeded in verifying Thomson's formula within 2.54

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[1] Edinb. Trans., 20, p. 283, 1883; Winkelmann, Handbuch der Physik, 2, Vol. 3, p. 637.

[2] Proc. Roy. Soc., 8, p. 353, 1857; Phil. Trans., 149, p. 91, 1859.

[3] Pogg. Ann., 126, p. 539, 1865.

[4] Dahlander, Pogg. Ann., 145, p. 147, 1872; Winkelmann, Hand. d. Phys., 2, Vol. 3, p. 60.

[5] Ann. d. Phys. u. Chem., 15, p. 1, 1882; Winkelmann, Hand. d. Phys., 2, Vol. 3, p. 637.

per cent. in the case of steel and within 0.25 per cent. in the case of german silver for changes of 21.715 and 17.134 kg. respectively in the stretching force.

Each of these investigators measured the change in the temperature of the wire by means of a thermocouple of which one junction was soldered to the stretched part of the wire and the other to an unstretched portion of the same wire. The disagreement in the results of investigations of this phenomenon are largely due to the difficulties involved in accurately measuring the small temperature changes. These changes are small, amounting to about 0.5° C. in the case of steel suddenly stretched to its elastic limit. But the quantity of heat liberated or absorbed is very small, owing to the small heat capacity of the metal wire, and this heat is so rapidly lost by surface conduction and radiation from the wire that the galvanometer, with its period of swing of several seconds, is unable to register the total initial change in temperature.

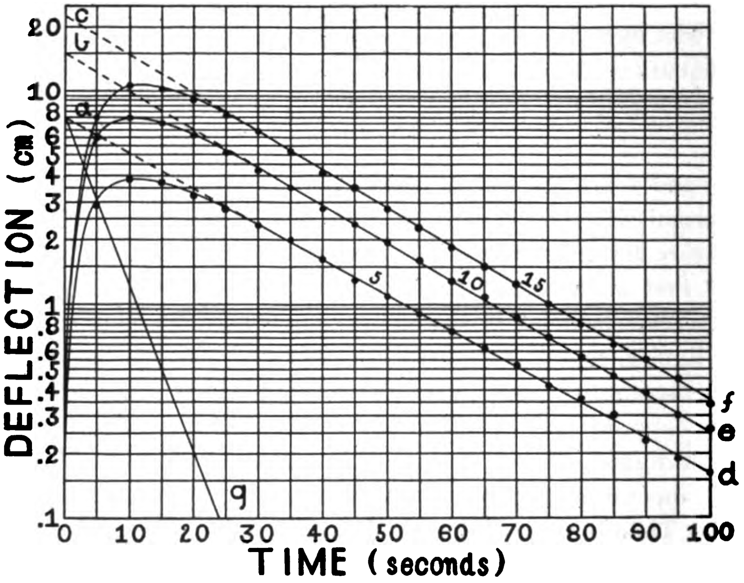

Fig. 1.

Haga employed a Thomson galvanometer whose period of swing was 6 seconds and whose damping factor was less than the critical value, so that it possessed an oscillatory swing. From the equation of motion of the galvanometer and observations of the first three swings following a change in the tension of the wire, he was able to calculate the deflection which would have been observed instantaneously after changing the tension if the inertia of the moving system of the galvanometer had been zero. To this was added an approximate correction for the deflection produced during the time (2 seconds) required to make the change in the tension. From the deflection thus calculated, the sensitiveness of the galvanometer, the resistance of the circuit and the constants of the thermocouple the initial change in the temperature of the wire could be calculated.

In the present investigation we discarded the thermocouple method of measuring the temperature change and employed a resistance method. The stretched wire formed one arm of a Wheatstone's bridge and the temperature change was calculated from the change in the resistance of the wire accompanying the removal of the stretching force. There are several features of this method which commend it as preferable to the thermocouple method. In the first place it is far more sensitive. A calculation of the current through the galvanometer when the bridge is thrown out of adjustment by a slight change in the temperature of the wire compared with the current which would be produced through the galvanometer by the same temperature change in an iron-platinum thermocouple shows that the resistance method may be made several hundred times more sensitive than the thermocouple method. In our apparatus the sensitiveness was about thirty-five times that of Haga's apparatus. In the second place the resistance method is free from possible errors due to the Peltier effect, which is a disturbing factor in all thermocouple work except that in which a balanced or potentiometer method can be employed. The Peltier effect would be of especial significance in this work, since the supply of heat near the junction is so minute. Such an error would tend to decrease the apparent temperature change, and is therefore in a direction to account for the fact that practically all the temperature changes observed by investigators have been smaller than those predicted by the theory. Finally, by using a strongly damped galvanometer, the computations were greatly simplified and instead of rather complicated calculations the results may be obtained graphically, as is shown later in the paper. The resistance method, however, can be employed only in the case of metals and then only for stretching forces so far within the elastic limit that there is no elastic lag. For this reason we chose steel piano wire as the material for investigation, and carefully tested it with a micrometer microscope to prove the absence of appreciable elastic lag within the region of the stretching forces which we employed.

Method.—One end of a steel piano wire was soldered into a heavy lug which was held rigidly in a clamp, while the other end was passed over a pulley and was attached to a constant weight of 2.5 kg. which maintained a taut horizontal length of 160 cm. of wire between the lug and the pulley. About 10 cm. from the pulley a short piece of No. 10 copper wire was soldered to the steel wire and dipped into a mercury cup. The lug and the mercury cup were the terminals of the 150 cm. length of wire which formed one arm of a Wheatstone's bridge. The balancing resistance was a calibrated standard 1.0050 ohm. The resistance of the bridge wire was 0.01032 ohm per cm., and this wire was extended by resistances of 40 and 41 ohms respectively at its ends. At room temperature, 24° C., the bridge balanced with the sliding contact at 68.0 cm., whence

$$R = 1.005\frac{41 + 68 \times 0.01032}{40 + 32 \times 0.01032} = 1.03918 \text{ ohms}$$

is the resistance of the steel wire. The battery terminals joined the two large to the two small resistances since this arrangement gave the largest deflections for a given current through the steel wire.

The galvanometer was calibrated with respect to temperature changes of the steel wire by the following simple method. The bridge was accurately balanced with the galvanometer at zero. A standard of 0.001 ohm resistance was then introduced in series with the steel wire. This caused the galvanometer to deflect 18.72 cm. Since the current through the galvanometer is proportional to the change in the resistance of one arm, if the change is small, we may consider each centimeter deflection as indicating a change $\Delta R = 0.00005345$ ohm in the resistance of the steel wire. Thus if a small change in the resistance of the wire is produced by a temperature change $\Delta\theta$, $\Delta R = R\alpha\Delta\theta$. We carefully determined the temperature coefficient of resistance α for the wire and found $\alpha = 0.002820$ ohm per ohm per degree at 24° C. Thus

$$1 \text{ cm. deflection} \simeq \frac{0.00005345}{1.03918 \times 0.002820} = 0.01825^\circ \text{ C.}$$

change in the temperature of the wire. There remains the problem of determining the deflection of the galvanometer, following a given change in the tension of the wire, which would occur if the galvanometer could respond *instantly* to temperature changes.

In order to reduce the rate of loss of heat from the wire it was passed axially through a polished tin tube whose ends were loosely plugged with cotton and which was covered with a thick layer of cotton to protect it from the effect of slight temperature variations in the room. This reduced the rate of loss of heat to less than half the rate when freely exposed.

After stretching the wire several times to avoid the anomalous effects of the first stretch the experiment was conducted as follows. The bridge was carefully balanced while the wire was kept taut by the constant tension of 2.5 kg. Then the galvanometer key was opened and the stretching weight added to the end of the wire. After standing several minutes the stretching weight was suddenly released by a snap and simultaneously the galvanometer circuit was closed and the deflections at five-second intervals were recorded. After the initial outward swing the galvanometer moved slowly back to zero as the wire cooled to room temperature. These readings were repeated five times each for changes of 5, 10 and 15 kg. respectively in the stretching force. The table of observations with five kg. shows the consistency of the results, especially after about ten seconds, when any effect of not pressing the galvanometer key exactly with the release of the weight becomes negligible. The logarithms of these averages, and also those for 10 and 15 kg., are plotted with the time in the accompanying figure.

Time Sec.	Deflection (Cm.).						Time Sec.	Deflection (Cm.).					
	1	2	3	4	5	Ave.		1	2	3	4	5	Ave.
0	0.00	0.00	0.00	0.00	0.00	0.00	65	0.60	0.60	0.65	0.65	0.60	0.62
5	3.10	2.00	3.20	3.40	2.90	2.92	70	0.50	0.50	0.55	0.55	0.50	0.52
10	3.95	3.65	4.00	4.00	3.70	3.86	75	0.40	0.42	0.45	0.45	0.40	0.43
15	3.80	3.60	3.80	3.80	3.50	3.70	80	0.35	0.37	0.40	0.40	0.30	0.36
20	3.30	3.30	3.30	3.30	3.05	3.25	85	0.30	0.30	0.30	0.35	0.27	0.30
25	2.80	2.80	2.85	2.80	2.70	2.79	90	0.23	0.24	0.23	0.28	0.20	0.23
30	2.40	2.40	2.40	2.40	2.20	2.36	95	0.20	0.20	0.18	0.22	0.17	0.19
35	2.00	2.00	2.00	2.00	1.90	1.98	100	0.15	0.18	0.15	0.20	0.15	0.16
40	1.70	1.60	1.65	1.60	1.50	1.61	110	0.14	0.10	0.10	0.15	0.10	0.13
45	1.30	1.30	1.30	1.35	1.20	1.29	120	0.10	0.08	0.10	0.10	0.05	0.09
50	1.10	1.10	1.10	1.10	1.00	1.08	130	0.05	0.00	0.05	0.05	0.00	0.03
55	0.90	0.90	0.90	0.90	0.85	0.89	140	0.00	0.00	0.00	0.05	0.00	0.01
60	0.75	0.75	0.75	0.80	0.70	0.75	150	0.00	0.00	0.00	0.00	0.00	0.00

The first deflections depend upon the moment of inertia and damping factor of the galvanometer as well as upon the rise in temperature of the wire. But after about thirty seconds the deflection at any instant accurately records the temperature of the wire at that instant, as is shown by the following analysis. Thus the curves after thirty seconds represent the cooling curves of the wire following these three changes in tension, and the points *a*, *b*, *c* at which these curves, extended, intersect the axis $t = 0$ give the deflections which would be recorded if the galvanometer could reach a steady deflection before the wire loses part of the heat developed.

The validity of this statement is proved by the solution of the equation of motion of the galvanometer,

$$I\frac{d^2x}{dt^2} + D\frac{dx}{dt} + Mx = ifM,$$

where x is the deflection, I is the moment of inertia and f the sensitiveness of the galvanometer, D is the moment of damping at unit rate of deflection, M is the moment of restoring force due to the suspension and i is the current through the galvanometer. The current at any instant t is given in terms of the initial rise in temperature θ_0, the resistance R of the wire and its temperature coefficient of resistance α and a constant k depending on the other resistances and the electromotive force in the bridge by

$$i = kR\alpha\theta_0 e^{-\frac{\sigma}{ms}t},$$

where σ is the thermal coefficient of surface conductivity of the wire and ms is its heat capacity per unit length. Putting

$$\frac{D}{I} = A, \qquad \frac{\sigma}{ms} = c,$$

$$\frac{M}{I} = B, \qquad \frac{2}{A - \sqrt{A^2 - 4B}} = T_1,$$

$$\frac{fMkR\alpha}{I} = C, \qquad \frac{2}{A + \sqrt{A^2 - 4B}} = T_2,$$

the equation reduces to

$$\frac{d^2x}{dt^2} + A\frac{dx}{dt} + Bx = C\theta_0 e^{-ct}, \tag{1}$$

of which the solution is

$$x = \frac{C}{C^2 - 2AC + 4B}\theta_0 e^{-ct} + c'e^{-\frac{t}{T_1}} + c''e^{-\frac{t}{T_2}},$$

where c' and c'' are the constants of integration.

The time constants T_1 and T_2 may be determined from the case where the right member of equation (1) is zero. To do this a portion of the bridge wire was short-circuited so that the galvanometer maintained a steady deflection at 7.5 cm. The short-circuiting key was suddenly removed and the readings noted at short intervals as the galvanometer returned to zero. The results are shown in the figure by the curve ag whose equation is

$$x = c_1 e^{-\frac{t}{T_1}} + c_2 e^{-\frac{t}{T_2}}.$$

T_1 is evidently too small to be detected (showing that the damping moment is very large compared with the restoring moment due to the suspension). It is certainly less than 0.5 second so that this component of the curve may be neglected. T_2 is the time taken for x to fall to $\frac{7{\cdot}5}{e}$, and is about 5.5 seconds. It is seen from the curve that the effect of this term is certainly negligible after 30 seconds.

Beyond thirty seconds, therefore, the deflection is given by

$$x = \frac{C}{C^2 - 2AC + 4B}\theta_0 e^{-ct} = x_0 e^{-ct}.$$

Thus the curves beyond 30 seconds represent the true cooling curves and the points a, b, c, at which these straight lines intersect the axis $t = 0$, are the true values of the initial deflections which would have been observed if the galvanometer had responded instantly to the initial currents.

The most probable straight line through the points beyond 30 seconds was determined in each of the three cases by the method of least squares and the probable error calculated. The three initial deflections a, b and c were thus found to be 7.5 ± 0.037 cm., 15.0 ± 0.047 cm. and 22.5 ± 0.056 cm. respectively. When these deflections are multiplied by the calibration constant 0.01825 we find that temperature changes of 0.1369° C., 0.2737° C. and 0.4106° C. were produced in the wire by changes of 5, 10 and 15 kg. respectively in the stretching force.

Comparison of Experiment with Theory.—In order to take into account possible variations in the thermal coefficient of linear expansion of the wire due to tension, we measured the coefficient of expansion between temperatures of 13.6° C. and 32.2° C. under tensions of 4.5, 7.0 and 9.5 kg., which were the average tensions in the three cases. The wire was passed axially through a cylindrical water jacket and the expansion was measured by micrometer microscopes. These results, together with the other constants of the wire are given in the following table:

Radius of wire	$r = 0.0310$ cm.
Density of wire	$\rho = 7.930$
Coefficient of linear expansion (4.5 kg.)	$a = 0.00001109$
(7.0 kg.)	$a = 0.00001111$
(9.5 kg.)	$a = 0.00001115$
Specific heat of wire	$s = 0.1178$
Room temperature	$\theta = 297.0°$ K.
Mechanical equivalent of heat	$J = 4.185\ (10)^7$
Acceleration of gravity	$g = 980.6$

The values of $\Delta\theta$ calculated from Thomson's formula by substitution of these quantities are given in the following table and compared with the experimental results. The theory is verified much more closely and consistently than heretofore. If the mean of the experimental results is used to calculate the mechanical equivalent of heat we find $J = 4.188\ (10)^7$ ergs per calorie. The best results for steel previously obtained (by Haga) lead to the value $J = 4.290\ (10)^7$ ergs per calorie, in which the error is about thirty-five times that in the present work.

F(kg.).	$\Delta\theta$ °C. (Calculated).	$\Delta\theta$ °C. (Observed).	Discrepancy, Per Cent.	Probable Error, Per Cent.
− 5.0	0.1366	0.1369	−0.22	±0.50
−10.0	0.2738	0.2737	+0.04	±0.32
−15.0	0.4122	0.4106	+0.39	±0.25
			Ave. = 0.07	

PHYSICAL LABORATORY,
REED COLLEGE.

THE ELECTRICAL, THE PHOTO-ELECTRICAL AND THE ELECTRO-MECHANICAL PROPERTIES OF CERTAIN CRYSTALS OF METALLIC SELENIUM, WITH CERTAIN APPLICATIONS TO CRYSTAL STRUCTURE.

By F. C. Brown.

OUR information concerning the structure of the atom has perhaps advanced faster of recent years than has our information about the larger unit which is composed of atoms. The phenomena of radioactivity which are fundamentally independent of crystal structure have in a large measure furnished the data for studies on the atom. In the end the facts about either unit will aid in the understanding of the other unit of matter. Bragg's studies[1] on the reflection of X-rays show the crystal structure to be made up of stationary parts. These parts indicate charges of electricity resting almost in a plane. I wish in this paper to correlate some notions about the atom and the crystal after I have related some experiments with crystals of metallic selenium which point toward a new departure as to the rôle of the conducting electron in matter. These crystals of selenium show many unique properties involving co-related phenomena of electrical, optical and mechanical nature, and it is because of these new phenomena that we have a possible opportunity of arriving at further advances in the electrical view of matter. There will be given reasons however for believing that these related phenomena are merely accentuated in selenium much as the magnetic properties are accentuated in iron.

Action at a Distance by Light.

Recently[2] it was shown that when light illuminated one part of a crystal that there was a consequent change of electrical conductivity throughout the crystal. The electrical effect was observed in one case 10 mm. away from the point of illumination, and the effect was apparently as large as if the illumination fell on a point only 0.5 mm. away. In the latter paper referred to it was shown that this electrical effect could even be transmitted from one crystal to another when the crystals

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[1] W. L. Bragg, Proc. Roy. Soc., *A*, 89, p. 248, and W. H. Bragg, Proc. Roy. Soc., *A*, 89, p. 277, 1914.

[2] Phil. Mag., Ser. VI, vol. 28, p. 497, and Phys. Rev., N. S., vol. 4, pp. 85 and 507, 1914.

were grown together. The essential difference between the direct action and the transmitted action as thus far observed is that the maximum effect for a given energy intensity is produced at longer wavelengths in the latter case. This shifting of the maximum sensibility was observed for 30-second exposures, which duration probably gave very nearly the equilibrium effect for a given intensity.

The action was, so far as could be observed, just as rapid when transmitted to a distance of 10 mm. as when transmitted only 0.5 mm. It thus can not be a mere temperature disturbance. Furthermore the major portion of the recovery after removing the light source was almost instantaneous.

When the crystal examined was illuminated at various points by a narrow beam of light it appeared that the light action was not uniform along the crystal. There were centers of varying sensibility. Thus the crystal has a mechanism of rather large dimensions, which when acted upon at different places produce results differing in magnitude.

The question that first arises is whether the equilibrium conductivity with a given illumination on a crystal represents an altered state of the crystal structure or whether it represents merely a condition in the crystal in which there is a constant liberation and supply of electrons that scatter throughout the crystal; the supposition being that for equilibrium the balance is kept up by the absorption of a similar quantity of electrons.

THE PRESSURE EFFECT IS NOT TRANSMITTED.

It has already been shown[1] that the conductivity of either the acicular or lamellar crystals may be increased several hundred times by the application of mechanical pressure. Also it was demonstrated in the same paper that the absolute change of conductivity by a given intensity of illumination increased proportional to the conductivity in the dark. Apparently the increased pressure on the crystal made it easier for the light to free the electrons. The view that is here being taken is that the greater the pressure the greater is the number of electrons existing in a state of equilibrium almost unstable. When in the dark it is these semi-fixed electrons that are transferred from center to center by electrical potential differences and it is also these that light acts upon and makes free of the atomic structure. Consequently the greater the number of these semi-stable electrons the greater will be the change of conductivity by a given illumination. This is a fairly simple explanation of the increased light-sensitiveness of the crystals when under high pressures. Of course later information may make this explanation purely a conventional one.

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[1] PHYS. REV., Ser. 2, Vol. 4, p. 85, 1914.

The above view was formulated to accord with the experimental result showing the pressure effect not to be transmitted to parts of the crystal not under pressure. The experiments were carried out as shown diagramatically in Fig. 1. The opposite ends, marked (1) and (2), of either a lamellar or an acicular crystal were placed between separate electrodes of brass. This apparatus permitted a number of experiments of varying character to be performed. If end (2) were illuminated the conductivity at end (1) changed almost as much as it did at the illuminated end. If the pressure were increased on end (2) the absolute sensibility to light increased almost proportional to the pressure, but the change of conductivity at (1) by illumination at (2) was not increased by this increase of pressure on end (2). However if the pressure were applied at (1) instead of (2), and the illumination just as above on end (1), then there was an increase in the absolute conductivity at (1).

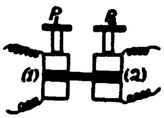

Fig. 1.

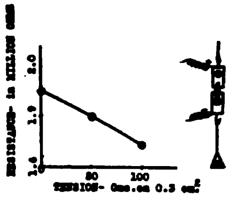

Fig. 2.

The conclusion is that the *pressure effect merely makes it easier for the light to change the conductivity and that the pressure does not act except at the point of application*. As will be pointed out elsewhere these results lead directly to the conclusion that pressure does not increase the conductivity by adding free electrons. And in view of the fact that the increased light-sensitivity due to high pressure is not transmitted we are justified in concluding that light does not produce free electrons in the generally accepted sense. In other words none of the conductivity in these crystals can arise from free electrons such as exist in metals according to the hypothesis of Richardson and Brown.

In the above experiment it was immaterial whether or not a current was flowing across both ends of the crystal simultaneously. A second set of experiments was made, with the same apparatus in such a way that the current flowed all the time through the part of the crystal under study and this same part of the crystal was not under pressure by the electrodes.

The pressure was applied simultaneously on both ends of the crystal. The essential part of the resistance was between the electrodes and this part of the crystal was obviously not under pressure. By varying the pressure on the crystal there was no change in the resistance. The electrodes were separated in different tests by distances ranging from 0.5 to 5 mm. In no case was there evidence that the change of resistance by pressure extended beyond the region under stress. Likewise the light-sensitiveness of the middle portion of the crystal did not increase as a result of the pressure on the ends.

Another related electro-mechanical effect is the change of resistance accompanying a stretching force. For the study of this effect five branch crystals growing out from a central spine such as reproduced in the earlier article were chosen. The opposite ends of these crystals were clamped in brass electrodes as shown in Fig. 2, so that the stress was distributed among the five crystals. The crystals were stretched by adding weights to a pan pulling on one of the electrodes as shown. This experiment was rather difficult because the apparent malleability of the crystals caused them to flatten out, tear and pull out of the clamps and also because the slightest twisting would cause the crystals to weaken and break. However I did succeed in observing that the crystals would withstand a stretching force greater than 10 kgm. per square centimeter. With such stresses there was a decided decrease of resistance as shown in the curve of Fig. 2. When the weights were removed the resistance usually increased again to its previous higher value without stress, thus indicating the crystal to be in equilibrium either with or without the additional forces.

The change of resistance for tensile forces does not seem to be as great as for compression forces as previously related. The interpretation that is to be placed on these results is that stress by stretching brings an increased number of electrons into almost unstable equilibrium and thus increases the current with a given potential difference. The fact that the effect is not so large as by compression forces may arise from an increasing of the distance between some of the semi-stable electrons, when this distance is measured in the direction of current flow.

THE ELECTRICAL CONDUCTIVITY WITH VARYING ELECTRICAL STRESSES.

On the preceding view of the structure of the crystal in which conducting charges are tied up in the atom in a quasi-stable condition, we should expect the number of electrons that could be dragged out of their fixed positions would vary with the electrical forces acting on them, and that only forces acting in the direction of current flow would alter the magnitude of the current. In what way the current should vary with the electrical forces will depend upon a more exact picture than we are yet able to formulate. When a lamellar crystal was under pressures only slightly greater than atmospheric, the resistance varied with increasing potential difference at the electrodes as shown in the lower curve of Fig. 3. The potential was applied in the direction of the current flow for about 20 seconds. For low potentials the change of resistance was almost steady after this time, but for high potentials, above 100 volts, there were signs of unsteadiness if the current were left on too long. Next the pressure was increased so that the conductivity increased twenty times in the dark, and the resistance was then observed to vary as shown by the upper curve in Fig. 3. At first sight one might be inclined to say that the change of resistance with varying electro-motive force is materially less with high pressure on the crystal. But inspection shows that only the percentage change is greater with low pressure. The following table gives the conductivity for some potential differences as deduced from the data graphed in Fig. 3.

Fig. 3.

Difference of Potential.	Conductivity in Dark.	
	With Low Pressure.	With High Pressure.
1.4 volts	3.84×10^{-8}	75.2×10^{-8}
10 volts	9.17×10^{-8}	83.3×10^{-8}
41 volts	14.3×10^{-8}	96.1×10^{-8}
100 volts	18.2×10^{-8}	98.0×10^{-8}
143 volts	19.6×10^{-8}	100×10^{-8}
Extreme variation in absolute specific conductivity	16×10^{-8}	25×10^{-8}

It is observed that the extreme variation of conductivity for the potentials used was somewhat greater with the crystal under high pressure than under low pressure. This merely signifies that the saturation current was not nearly reached by increasing the conductivity by a factor of twenty. The increased pressure probably makes the electrons free to leave the atomic structure with lower potentials. The instability of the electrons is increased by either mechanical pressure or electrical stresses.

Light-sensitiveness with Different Potentials.—If light produces free electrons and the electrical stress merely pulls electrons out of the atomic structures in the line of conduction, we should expect that the conductivity by illumination would be increased by the same amount regardless of the potentials across the crystal. This is on the supposition that the conductivity increases proportional to the increase in the number of conducting electrons, and that the stability of the fixed electrons in no wise determines how many are to be freed by light.

The following table gives the results that were obtained to check the validity of the above, when the crystal was illuminated with light of constant intensity until equilibrium was reached.

Potential Fall Across Crystal.	Resistance.		Ratio of $\frac{\text{C in Dark}}{\text{C in Light}}$.
	In Dark.	Illuminated.	
1.4 volts	1.30×10^6	$.82 \times 10^6$	
	1.20 "	.80 "	
	1.20 "	.79 "	
	1.20 "	.79 "	
	1.20 "		1.53±.03
60 volts	$.475 \times 10^6$	$.299 \times 10^6$	
	.475 "	.310 "	
	.49 "	.323 "	
	.492 "	.325 "	
	.495 "	.330 "	1.53±.02

It is observed that the percentage increase of conductivity is the same regardless of what the initial conductivity may be as influenced by the potential fall across the crystal. But this means that the absolute increase of conductivity is nearly three times greater with the higher voltage. Therefore the presumptions mentioned above are not true. The exactness of the ratio of the increase of conductivity would favor the view that the light renders a constant number of electrons in a quasi-stable equilibrium, and that the apparent increased sensibility by using higher potentials is merely the result of a pulling out of a greater number of semi-stable electrons.

It should be noted that the constancy of the light-sensibility ratio above shown for electrical potentials is identical to the result noted in my previous paper[1] where the percentage increase of conductivity by illumination remained constant for varying pressures. No doubt the two sets of results have an analogous explanation and this leads to the suggestion that electrical stresses and mechanical pressures alter the equilibrium of the crystal structure in identical ways.

The Non-transmissibility of the Electrical Potential Effect.—If the above identity exists we should expect that the effect of high potentials should alter the conductivity only on that part of the crystal in the immediate field the same as found for the pressure effect. Two experiments were carried out in a fairly satisfactory manner to answer this question.

In the first experiment one end of an acicular crystal was placed

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[1] Loc. cit.

between electrodes differing in potential by 1.4 volts. The exterior circuit was closed through a galvanometer as shown in Fig. 4. The deflection of the galvanometer was noted. Then a potential difference of 100 volts was applied across the opposite end (*B*) of the crystal. This high potential changed the conductivity of end (*B*) by about a factor of five, but there could not be detected the slightest change of conductivity at the end *A*, as result of the potential effect, even when the opposite sets of electrodes were approached within one millimeter of each other. It should also be noted that there was no permanent potential generated at (*A*) by the application of the high potential at (*B*). Such a potential would have been indicated by the galvanometer.

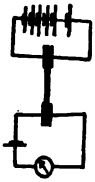

Fig. 4.

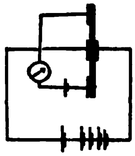

Fig. 5.

The second experiment was designed to detect any effect by an electrical stress acting at right angles to the current flow. The high potential was applied across the middle of the acicular crystal as shown in Fig. 5. The conductivity was being measured by a current flowing lengthwise of the crystal. However a strip of mica on one of the middle electrodes prevented the flow of a current by the high potential of 200 volts.

The result of this experiment was also negative. These two experiments show that a selenium crystal may change its resistance along one axis without altering the resistance along a perpendicular axis. This result is explicable on the view that free electrons are not the current bearers in non-illuminated selenium.

It may be that the piezo-electric effect, as exhibited for example in quartz where a number of electrons are freed by pressure, bears a certain resemblance to the effect described above. The quartz perhaps does not show a corresponding change of resistance because of its extreme insulating properties.

CONCLUSIONS.

It has been shown, (1) when a selenium crystal is illuminated at certain points that the conductivity of the entire crystal is increased, (2) that when pressure is applied to the crystal only that part of the crystal under pressure is altered, (3) that electrical forces alter the conductivity only of that part directly under the forces and further that the influence is exerted only in the direction of the electrical force.

The direct conclusion is that light action has to do with an essentially different mechanism than electrical stresses or mechanical stresses. Starting with the above fundamental facts and correlating the other facts mentioned in the paper, I have attempted to formulate certain notions about the structure of the crystal.

This notion premises that a crystal when in the dark has no free electrons in the ordinary sense such as was found to exist in certain metals by the hypothesis and experimental work of Richardson and Brown.[1] True a crystal conducts electricity when in the dark, but this conductivity is small compared with that of the metals. The elementary notion of the crystal is merely a structure composed of positive and negative charges in equilibrium with each other. But this equilibrium is for a large number of the electrons at least in a very low degree of stability. The electrons would be held in equilibrium by the positive forces essentially, but certain of them while necessary to the complete atomic structure, would nevertheless leave the centers (*i. e.*, perhaps atoms) when under small stresses. So long as an electron remains outside an atom requiring one or more electrons, this electron would behave as the traditional free electron. Thus whatever makes free electrons would increase the conductivity.

The hypothesis is that the conductivity in the dark does not arise from the free electrons, except those that have not had time to adjust themselves following an internal disturbance, but from electrons that are pulled from one atom to the neighboring atom and so on by the electrical forces across the crystal. The following is evidence for this view; first it was noted that for very small electromotive forces the resistance was almost infinite and for increasing potentials up to a certain limit the resistance decreased very rapidly. Secondly, it was noted that very large potential differences acting at right angles to the current flow did not alter the magnitude of the current.

The pressure effect is readily explicable on the basis that no free electrons exist in the crystal when in the dark. Pressure may increase the conductivity many hundred fold, but it will not influence the resistance outside the part of the crystal pressed upon. It would seem then that mechanical pressure merely pushes the electrical charges, associated with neighboring atoms, into a less stable equilibrium, perhaps closer proximity, so that a given electrical stress can pull more electrons from one atom to the next.

We are now in a position to assert something concerning the nature of light-action, based on the fundamental property of transmitted action.

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[1] Phil. Mag., Ser. VI, 16, p. 353, 1908.

By some mechanism the light can, no doubt because of its electromagnetic properties, lower the degree of stability of many or all of the electrons throughout the crystal. These same electrons may have their degree of stability yet further lowered by mechanical pressure. The lower the average stability of the electrons the greater will be the current with a given potential difference. With a greater potential difference the same light intensity would therefore seem to produce a greater change of conductivity. The electrons after removal from their fixed positions may behave, until reunited in the structure, somewhat as the traditional electron.

The action of light is not local. The electrons are made less stable or temporarily free by an indirect mechanism operating everywhere in the crystal. The effect is almost uniform at all points. It travels too fast to be a temperature transmission and the maximum sensibility for the transmitted action is in the visible spectrum. The transmission is at least analogous to that of a mechanical vibration, although only certain parts of the crystal may take part in its operation.

The reader will observe that aside from the experimental work the essential new thought in this paper is a new hypothesis to explain the nature of electrical conduction in certain crystals. This hypothesis bears some resemblance to the accepted theory of electrolytic conduction, the distinctive feature being that only electrons move from one center to the next in the chain of centers between electrodes. This view requires that the crystal shall have fixed electrons in its structure but no permanently free electrons.

The Physical Laboratory,
The State University of Iowa.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SEVENTY-FIFTH MEETING.

A REGULAR meeting of the Physical Society was held in Randall-Morgan Laboratory of the University of Pennsylvania December 29, 1914, to January 1, 1915. It was a joint meeting with Section B of the American Association for the Advancement of Science. Morning and afternoon sessions were held on Tuesday, Wednesday, and Thursday. Vice-President Anthony Zeleny of Section B presided on Tuesday and Wednesday afternoons, and President Merritt at the other four sessions.

On Tuesday afternoon the program consisted of the vice-presidential address before Section B on "Recent Evidence for the Existence of the Nucleus Atom" by A. D. Cole and the presidential address of the American Physical Society on "Luminescence" by Ernest Merritt. On Wednesday afternoon there was a symposium on the Use of Dimensional Equations, led by E. Buckingham, who was followed by A. C. Lunn, A. G. Webster, W. S. Franklin, and others.

The following program of papers was presented:

An A. C. Bridge for the Measurement of the Dielectric Loss and Dielectric Constant at High Voltages and Low Frequencies. CHESTER A. BUTMAN.

Influence of the Concentration of Electrolyte upon Electrode Potentials. ARTHUR W. EWELL.

A New Method of Obtaining a Hysteresis Loop. W. N. FENNINGER.

On Rotation and Magnetization. S. J. BARNETT.

Note on Thermo E.M.F.'s in which the Resultant Peltier Effect is Zero. H. C. BARKER.

Linear Resistance Change with Temperature of Certain Molten Metals. E. F. NORTHRUP.

The Effect of Temperature on the Dielectric Strength, the Dielectric Loss and the Dielectric Constant of Paraffine Oil. CHESTER A. BUTMAN.

A Preliminary Note on the Variation of Stray Power Losses in a Dynamo. W. N. FENNINGER.

Relation Between the Energy of the Cathode Rays and the Frequency of the X-Rays Produced by Them. WILLIAM DUANE.

Thermionic Currents from a Wehnelt Cathode. W. WILSON.

Mobility of Ions at Different Temperature and Constant Gas Density. HENRY A. ERIKSON.

The Radioactive Content of Certain Minnesota Soils. **James C. Sanderson**, read by **H. A. Erikson**.

Conducting Gas Layer at a Metallic Surface. **G. W. Stewart**.

X-Rays From the Electrical Discharge. **Elizabeth R. Laird**.

X-Rays Produced by Slow-moving Cathode Rays. **Elizabeth R. Laird**.

Light Due to Recombination of Ions. **C. D. Child**.

Electric Furnace Evidence on the Relation of Spectrum Lines Having Constant Differences in Wave-Number. (By title.) **Arthur S. King**.

The Mechanical Equivalent of Light. **H. E. Ives, W. W. Coblentz**, and **E. F. Kingsbury**.

Fluorescence of the Uranyl Salts under X-Ray Excitation. **Frances G. Wick**.

The Efficiency of Energy Transformation in the Corona Method of Precipitating Fumes. **W. W. Strong**.

Leakage of Gases Through Quartz Tubes. (By title.) **E. C. Mayer**.

A New Method for Measuring Gravity at Sea, with Some Trans-Pacific Observations. **Lyman J. Briggs**.

The Oxidation of Nitrogen. **W. W. Strong**.

The Alleged Dissymmetrical Broadening of the D Lines of Sodium. **E. A. Eckhardt**.

Exhibit of Mechanical Models Illustrating (*a*) Subdivision of Alternating Current Between Two Branches in Parallel, (*b*) The Alternating Current Transformer, (*c*) Coupled Circuits in Wireless Telegraphy. **W. S. Franklin**.

Some Causes of Variation in the Sensitivity of Moving Coil Galvanometers. **Paul E. Klopsteg** (presented by **A. Zeleny**).

A New Standard Phone and Phonometer for any Pitch. **A. G. Webster**.

A New Form of Radiation Pyrometer. (By title.) **S. Leroy Brown**.

The Doppler Effect in X-Ray Spectra and Application to the Kinetic Theory of Solids. **L. Gilchrist and D. A. Keys**.

On Acoustic Impedance, and an Approximate Theory of Conical Horns. **A. G. Webster**.

Vapors with Positive Specific Heat in Energy Conversion. (By title.) **J. E. Siebel**.

Progress of B-Particles through Matter. **A. F. Kovarik and L. W. McKeehan**.

A Thirty-two Element Harmonic Synthesizer. **Dayton C. Miller**.

The Result of Plotting the Separation of Homologous Pairs against Atomic Numbers instead of Atomic Weights. **Herbert E. Ives and Otto Stuhlmann**.

Beaded Lightning. **W. J. Humphreys**.

A Practical Measurement of Colors. **H. E. Wetherill**.

Preliminary Note on a Mercury-vapor Tube Oscillator. **B. Liebowitz**, introduced by **M. I. Pupin**.

On Tuesday evening a public lecture, complimentary to the citizens of Philadelphia and illustrated by experiments and the lantern, was given by

Dayton C. Miller. On Wednesday evening a successful dinner for Physicists was arranged by Professor H. C. Richards at a hotel near the University. This was enjoyed by about seventy members. The members of the Society were the guests of the University of Pennsylvania at lunch each day of the meeting. The registration of the meeting was one hundred and seventeen. The attendance at the various sessions was exceptionally uniform and varied between one hundred and one hundred and fifty.

The result of the mail ballot for officers for 1915 was announced at the meeting as follows: For President Ernest Merritt, vice-president K. E. Guthe, secretary A. D. Cole, treasurer J. S. Ames; for members of Council (three years) C. E. Mendenhall and G. W. Stewart, and for Editorial Board J. S. Ames, A. A. Michelson and E. Buckingham. The reports of the managing editor of the PHYSICAL REVIEW was presented by the editor. It was approved and that of the treasurer reported in the hands of the President, duly audited. Both were ordered printed, to be sent to each member with the announcement of next meeting.

A. D. COLE,
Secretary.

A METHOD OF DETERMINING WHETHER OR NOT THE VELOCITY OF LIGHT DEPENDS UPON THE VELOCITY OF THE SOURCE, BY THE USE OF CANAL RAYS.[1]

BY GORDON S. FULCHER.

LET a source of light, a canal ray for instance, move toward an observer, that is a spectrograph, with a speed v with reference to a system in which the speed of light is c, while the observer is moving toward the source with a speed u with reference to the same system so that the relative speed is $v + u = V$. If the source s and observer o are at a distance apart equal to l at the instant $t = 0$, the 1st and the $(n+1)$th waves will reach the observer at instants $l/(c + u)$ and $1 + (l - u - v)/(c + u)$, if the source sends out n waves per second. The observer receives n waves in the time

$$1 + \frac{l - u - v}{c + u} - \frac{l}{c + u} = \frac{c - v}{c + u}$$

or at the rate of $n[(c + u)/(c - v)] = n'$, per second. The resulting doppler effect would be

$$n' - n = n\frac{v + u}{c - v} = n\frac{V}{c - V + u}.$$

Now suppose the apparatus rotated through 180° so that the relative speed of the source with reference to the observer is the same as before, but the speed with reference to the fixed system is greater. The number of waves received per second by the observer now is

$$n'' = n\left(\frac{c - u}{c - v}\right);$$

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 28, 1914.

the doppler effect would be

$$n'' - n = n\left(\frac{uv - ,}{c - v}\right) = n\,\frac{V}{c - V - u}.$$

Supposing the two spectrograms are taken one immediately above the other the shift in the doppler effect which should be observed if, as we have assumed, the velocity of light in the fixed medium is independent of the velocity of the source, is

$$n'' - n' = n \cdot \frac{2uV}{(c - V)^2 - u^2};$$

or, approximately,

$$\Delta\lambda = \frac{\lambda_1^2}{\lambda} \cdot \frac{2uV}{(c - V)^2} = \lambda \cdot \frac{2uV}{c^2}.$$

If $u/c = 10^{-4}$ (earth); $V/c = 10^{-2}$ (fastest canal rays); $\lambda = 4861$ Å (H_β); then $\Delta\lambda = 2 \times 10^{-6}\,\lambda = .0097$ Å. To measure this, we should require very homogeneous, parallel, canal rays whose high speed must be maintained constant within one part in 10,000 during the experiment. While the experimental difficulties would be very great, they do not seem insurmountable.

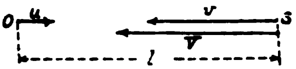

Fig. 1.

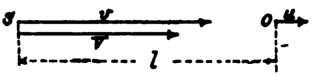

Fig. 2.

It is to be noted that the shift is a first order change of the doppler effect and can not be accounted for, if it is found by experiment to exist, by any second order change of V or l. The wave-lengths are measured in all cases by a spectrometer moving with the same speed with reference to the fixed system.

University of Wisconsin,

Note on Thermo E.M.F.'s in Which the Resultant Peltier E.M.F. is Zero.[1]

By H. C. Barker.

TAIT and others have noted that couples having two or more neutral points would give thermoelectric currents maintained by the Thomson effect alone, if the junctions were at the temperatures of the neutral points.

In this case the resultant Peltier E.M.F. is zero as the component Peltier E.M.F.'s are each equal to zero.

The writer has been led to question whether it is generally recognized that the Thomson thermodynamic theory leads to the conclusion that large thermo E.M.F.'s in which the resultant Peltier E.M.F. is zero, are obtainable with couples for which there exists only one neutral point.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

The condition is easily shown to be that the sum of the junction temperatures be equal to the neutral temperature. The Peltier E.M.F.'s are then equal, and their difference, the resultant Peltier E.M.F., is zero. Thus the current may be said to be maintained by the Thomson effect alone.

It is plain that two temperatures meeting this condition may be so chosen that the thermo E.M.F. is relatively large.

The appended curves exhibit the essential relations.

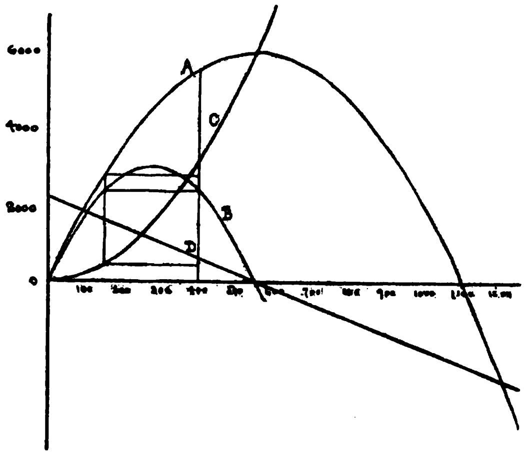

Fig. 1.

Abscissæ represent absolute temperature. Ordinates for curves *A*, *B* and *C* represent E.M.F. in microvolts. Ordinates for Curve *D* represent microvolts per degree, × 100.

Curve *A*. $E = 22\theta - .02\theta^2$. Thermo E.M.F. is given by difference in ordinates.

Curve *B*. $e_p = \theta \frac{\partial E}{\partial \theta} = 22\theta - .04\theta^2$. Resultant Peltier E.M.F. given by difference in ordinates.

Curve *C*. $e_T = -\int_0^\theta \theta \frac{\partial^2 E}{\partial \theta^2} d\theta = .02\theta^2$. Resultant Thomson E.M.F. given by difference in ordinates.

Curve *D*. $P = \frac{\partial E}{\partial \theta} = 22 - .04\theta$. Thermoelectric power.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA.

LINEAR RESISTANCE CHANGE WITH TEMPERATURE OF CERTAIN MOLTEN METALS.[1]

BY EDWIN F. NORTHRUP.

COPPER and tin have been studied to 1680° C., lead to over 1600° C., gold to 1500° C., silver to 1340° C., bismuth to 750° C. and their change of resistance with temperature when molten has been found, within the limits

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

of accuracy of the measurements, to be linear. Lead and tin, particularly the latter, are shown to constitute excellent thermometric materials for the accurate measurement of high temperatures which may be read with apparatus that reads on a uniformly spaced scale directly in degrees centigrade. Several features and relations of interest respecting the resistivities of the above metals are pointed out.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

INFLUENCE OF CONCENTRATION OF ELECTROLYTE UPON ELECTRODE POTENTIALS.[1]

BY ARTHUR W. EWELL.

ACCORDING to Nernst's formula, the potential of an electrode dipping into an electrolyte increases as the concentration of the electrolyte is increased. At ordinary temperatures the amount of increase is $.058/N \log c_2/c_1$ where N is the valency and c_2/c_1 is the ratio of the concentrations. This law has often been closely verified by well-known electrochemical methods, both when the electrode dips in the electrolyte and when the two are separated by ionized air.

A year ago Borelius showed that when single electrode potentials were studied electrostatically the potential decreased as the concentration was increased, the rate of decrease being approximately equal to the rate of increase hitherto observed.

The writer has studied the influence of concentration, employing a modification of the apparatus recently used for determining absolute single potentials.[2] The two electrolytes of different concentrations were contained in two similar glass flasks. The silver film on the outside of each was connected to a pair of quadrants of a Dolezalek electrometer and the deflections of the latter were observed when earthed electrodes were dipped into the electrolytes. The observations gave values for the numerical factor (.058 in Nernst's equation) between .037 and .053 and all negative, thus confirming Borelius's results with a type of apparatus which, unlike Borelius's apparatus, gave absolute potentials independent of Volta effects.

WORCESTER POLYTECHNIC INSTITUTE.

THE ALLEGED DISSYMMETRICAL BROADENING OF THE D LINES OF SODIUM.[1]

BY E. A. ECKHARDT.

H. KAYSER in his Handbuch der Spectroscopie[3] refers to the dissymmetrical broadening of the D lines in an emission spectrum. Bro-

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

[2] This Journal, Vol. IV, No. 6, p. 547.

[3] H. Kayser, Handbuch der Spectroscopie, Vol. II, p. 365.

therus[1] and Iwanow[2] as well as others appear to have subsequently observed the same phenomenon. The present investigation had for its program first the reproduction of this dissymmetrical broadening and then by measurably controlling the factors which are responsible for the broadening to find if possible in what manner the dissymmetry is introduced.

Since the dissymmetries seem always to have been observed in emission spectra it seemed pertinent to investigate whether they exist also in the corresponding absorption spectra. Consequently the light of an arc lamp was made to pass through a strongly absorbing sodium flame and was then focused on the slit of a grating spectroscope. The absorption of the sodium flame was under control within very wide limits. The spectrum was photographed and the distribution of intensity across the spectrum lines was determined by means of a Hartmann photometer.

Although the D lines were broadened much more than they had been in the experiments of Brotherus and Iwanow no dissymmetries of any kind were discovered. The results of the present work indicate strongly that there are no dissymmetries in the absorption spectrum obtained under conditions which are comparable to those in which the dissymmetry has actually been observed in the emission spectrum. If the dissymmetries really exist in the emission spectrum, they appear to have no counterpart in the corresponding absorption spectrum. The work could not be completed because the Hartmann photometer which had been borrowed ceased to be available. It is hoped that the original program may be carried to its conclusion in the near future.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA.

IONIZATION AT METALLIC SURFACES.[1]

BY G. W. STEWART.

WE have much evidence that suggests ionized layers of gas at metallic surfaces at atmospheric pressures, but only the experiments of Anderson and Anderson and Morrison furnish direct evidence.

The apparatus consisted of two polished surfaces, one silver and one german silver, .35 cm. and .50 cm. in diameter respectively. These are plane to within one half wave-length of light. They are approached by an interferometer carriage. Distances were measured by electrical capacity method and by the screw of instrument.

The experiments argue in favor of an ionized layer of gas because of the following points:

1. The minimum distance of approach without apparent conduction was four wave-lengths. Without an ionized layer this distance would have been one wave-length.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

[1] Hj. V. Brotherus, Ann. d. Phys., Ser. 4, 38, 1912, p. 416.

[2] K. Iwanow, Phys. Z., XIII, 1912, p. 1118.

2. With air, oxygen and hydrogen, the presence of water vapor extends the layer ten to forty wave-lengths.

3. Effect of the three gases named and carbon dioxide is similar, but probably not the same. The influence of water vapor in the case of the latter is less distinct and may not exist at all.

4. Current-voltage curves taken of necessity without the existence of steady states, indicate either ionization by collision or the dragging of additional ions from near the surface by the increased voltage.

5. An approximate value of the contact potential difference is obtained by virtue of the ionized layer.

6. The current-voltage curves shift with direction of field in accord with the contact potential difference value.

The surface layer is found in both of the metals used. Moreover, this layer explains well-known facts with insulators. The origin of the ionization is not clear. It is improbable that it is due to the electrons from within or to a radioactive impurity now known. More probable causes would be the intrinsic radiation of the metal, an unknown radioactive impurity, and chemical action.

The presence of ionized layers of gas is important in the study of coherer action, carbon transmitter action, double layer electrification at low pressures, and the ionization supposed to be due to a penetrating radiation.

The State University of Iowa,
Iowa City, Ia.

Light Produced by Recombination of Ions.[1]

By C. D. Child.

CERTAIN phenomena connected with the luminosity of the light rising from the mercury arc indicate that this light is produced by the recombination of ions.[2] If this explanation is correct, the light must continue for a time after the current through the arc has been stopped. This can be tested by observing the light from an alternating current arc at different phases of the current. Such observations have already been made for the carbon arc in air by Fleming and Petavel[3] who found that the light from the gas between the carbons does not disappear entirely at the time when the current is zero.

Since the phenomena with the carbon arc in air is complicated by the oxidation of the carbon and by the high temperature of the gas, it seemed desirable to repeat their experiment substituting mercury terminals in a vacuum for carbon terminals in the air. This has been done and it has been found that in this case also the light continues to exist for an appreciable length of time after the current has ceased flowing. Such light can not be due to ionization and is in all probability due to recombination of the ions.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society. December 29–31, 1914.

[2] Phil. Mag. (6), 26, 906, 1914.

[3] Phil. Mag. (5), 41, 339, 1896.

Measurements are now being made for the purpose of learning the length of time that the light continues after the current ceases and the rate at which the light dies away.

COLGATE UNIVERSITY,
HAMILTON, N. Y.

A NEW METHOD FOR MEASURING GRAVITY AT SEA, WITH SOME TRANS-PACIFIC OBSERVATIONS.[1]

BY LYMAN J. BRIGGS.

THE apparatus used was in principle similar to a closed barometer. The air-chamber consisted of a closed glass tube 3 cm. in diameter and 60 cm. long. A capillary tube was sealed into the upper end of the air-chamber and extended nearly to the bottom of the latter, the lower end opening beneath a mercury surface. The capillary above the air-chamber was bent into a zigzag glass spring and ended in a spherical bulb 3 cm. in diameter. This bulb contained a fixed ground glass point extending to the center of the bulb with its axis forming an extension of the axis of the air-chamber. The bulb was mounted in a light carriage sliding on rods clamped to the air-chamber. A micrometer-screw mounted on the rods above the carriage controlled the position of the carriage and bulb. The bulb was highly evacuated and sealed off. The whole apparatus was then packed in crushed natural ice, and the air-pressure in the chamber adjusted until the mercury stood in contact with the glass point. The air-chamber was then sealed off.

As long as the apparatus is vertical and is surrounded by and in equilibrium with pure melting ice, a change in the height of the column is theoretically dependent only on a change in the force of gravity, provided the apparatus is assumed to be free from volume-changes due to external pressure. The height of the bulb is so adjusted by means of the screw that at the time the final reading is made the mercury surface is barely in contact with the glass point. Under these conditions the quantity of mercury remaining in the air-chamber is always the same. The apparatus is, therefore, of the constant-volume type, and the height of the mercury column at two stations is inversely proportional to the force of gravity.

The length of the column is such that when the apparatus is removed from the ice tank, the upper bulb becomes completely filled with mercury. The apparatus may then be tipped in any position and is perfectly transportable. On board ship, the cork-covered ice tank containing the apparatus was swung from gimbals, the latter being suspended from spiral springs.

In the laboratory, a series of readings made on different days agreed to within less than 1 part in 200,000. On board ship, however, things happen that the writer at least did not anticipate, and which combine to reduce the accuracy to 1 part in 50,000, or even less, depending on the weather and the ship. The

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

apparatus is now being modified with the hope of increasing the accuracy of measurements at sea.

U. S. Bureau of Plant Industry,
Washington, D. C.

Leakage of Gases Through Quartz Tubes.[1]

By E. C. Mayer.

A CYLINDRICAL tube of quartz closed at one end of approximately 51 cu. cm. volume and 111 sq. cm. internal superficial area, was found to be pervious to hydrogen at temperatures ranging from 330° C. to 710° C., and at pressures varying from 20 cm. below to 20 cm. above atmospheric pressure. The quartz was of the transparent variety. The curve indicates the general character of the results. Time in minutes is plotted as abscissas, and lengths proportional to volume of gas reduced to 15° C. and 76 cm. pressure as ordinates. Each unit of the ordinate scale corresponds to a volume of 0.217 cu. cm. In the case of oxygen and nitrogen, no leakage could be detected for pressures less than one atmosphere. Nitrogen did not seem to escape until a temperature of about 430° C. was obtained. At constant temperature the results for all gases showed a considerable increase in leakage with increasing pressures. Under approximately like conditions hydrogen leaks most rapidly and nitrogen least.

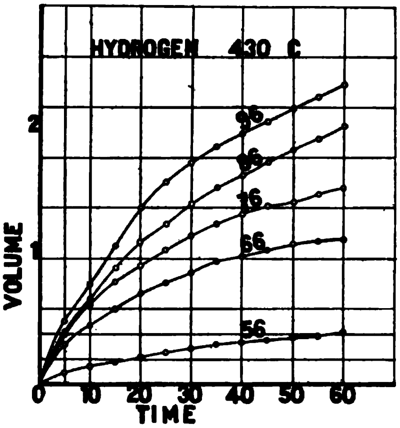

Fig. 1.

Heating was obtained by means of an electric furnace. Temperature was measured by an iron-advance thermocouple.

Cornell University,
Ithaca, N. Y.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

NEW BOOKS.

Chemistry. By Georges Darzens. New York: Doubleday, Page and Company, 1914. Pp. viii+122.

Mechanics. By C. E. Guillaume. New York: Doubleday, Page and Company, 1914. Pp. xiii+199.

These two volumes belong to "The Threshold of Science" series which, as is well known, met with immediate success in France where it was first published. If one may form an opinion of the whole series from the two volumes before us its success on this continent will be equally great. The monographs "Chemistry" and "Mechanics" are written in a most attractive style by men of eminence. They have been brought out to meet (1) the need of the man who would teach himself the elements of chemistry and mechanics and (2) the need of young people who are showing themselves increasingly eager to acquire a knowledge of the principles underlying these and other branches of science. The books are well illustrated and are issued at the cheapest possible price.

J. C. M.

Die Polhöhenschwankungen. By Dr. E. Przybyllok. Braunschweig: Vieweg and Sohn, 1914. Pp. 1+41. Price, 1.60 Mk.

The "Sammlung Vieweg" of which the present volume forms the eleventh number has the aim to present in concise form a discussion of scientific problems which, at the present, cannot be considered as having been solved satisfactorily. These volumes are of moderate size, contain references to the more important publications on the subject and thus greatly facilitate a general orientation in a given field. The book here reviewed is a characteristic example.

Increased accuracy of astronomical observations has proven the existence of periodic variation of latitude, or, a shifting of the earth's pole. This was suspected by Bessel as early as 1844 and clearly shown to be the case by Chandler forty years later. In 1889 the solution of the problem was undertaken by the International Geodetic Association and since then continuous, systematic observations have been made in a number of suitably located observatories. But the causes for the now fully recognized and accurately determined periodic variations of latitude have not yet been satisfactorily explained. Przybyllok gives an interesting account of the historical development of the problem and the results so far obtained.

K. E. G.

Principles of Physics. By W. E. Tower, C. H. Smith and C. M. Turton. Philadelphia: P. Blakiston's Son and Co., 1914. Pp. xi+466.

This is a high school text written by three experienced high-school teachers. Throughout the book the authors have been true to their conviction that—to quote from the preface—"the most efficient teaching in physics involves a departure from the quantitative, mathematical methods of presentation—toward a method better adapted to the capabilities, interests, and requirements of the young people." In common with other modern high-school texts the discussion of force and motion is given after mechanics of liquids and gases. The chapters on sound and light follow those on electricity and magnetism. The subject matter and its treatment does not differ materially from that found in other books of this kind. The style is simple and clear, applications to common, everyday experiences are frequent and the illustrations faultless.

K. E. G.

Kräfte und Spannungen; Das Gravitations- und Strahlenfeld. Max B. Weinstein. Braunschweig: Vieweg und Sohn, 1914. Pp. vi+64. Price, M2.

This is the eighth of the Vieweg series of pamphlets on pending questions in science, and is designed to give a concise account of modern theories of force, meaning thereby chiefly those which have grown out of Maxwell's theory of surface stresses, and which are closely related to the recent theory of relativity.

Following some introductory remarks on causality, atomistic theories, and a few mathematical definitions, the first half of the book is devoted to Maxwell's original formulas for the electromagnetic stresses, to the analogous four-dimensional theory developed by Minkowski, and to the modifications suggested by Hertz, Abraham, and others; the latter half is devoted to forces in their purely mechanical aspect and to the recent theories of gravitation, which are so intimately related to electromagnetic theory and the principle of relativity. The treatment is summary in form, and emphasis is placed chiefly on the formulation of theories, with only occasional reference to physical interpretation or experimental test.

The subject is both fascinating and perplexing, and such a birds'-eye-view will be interesting to readers who are familiar with vector analysis, electromagnetics, and the Einstein-Minkowski theory, to whom alone it is likely to be fully intelligible. Though published independently, the book may be considered a natural supplement to the author's recent volume on the physics of moving matter.

A. C. L.

Experiments. By Philip E. Edelman. Minneapolis: Edelman, 1914. Pp.. 1+256. Price, $1.50.

This book is dedicated to "all who are interested in progress." It contains a large number of experiments in the fields of chemistry, current electricity, wireless telegraphy, horticulture, etc. It closes with about fifty pages of a general discussion on science and invention, and "research." Characteristic topics are such as the building of small motors, transformers, of stations for wireless telegraphy, X-ray experiments, experimental aeronautics. Those who wish to play with science will find in the book many practical hints and by its use may be led to a desire for a deeper and broader knowledge of the subjects presented in the book.

K. E. G.

Dynamische und Statistische Gesetzmässigkeit. By Max Planck. Leipzig: J. A. Barth, 1914. Pp. 1+31. Price, 1 M.

The distinguished author of this address, delivered at the celebration in memory of the founder of Berlin University, discusses for a general audience the points of contrast between the applications of the dynamical and the statistical methods in science. He points out that in physics the application of the statistical method is justified by the demonstration of the atomic hypothesis given by the study of the Brownian movements. He calls attention to the possibility of the occurrence of events of which the probability is small, and illustrates his general statements by interesting examples. When considering the necessity of inquiring, whenever a law or regular procedure in nature is demonstrated, whether the law observed has a dynamical or a statistical basis, he asserts that, in the final thought on even the statistical problem, an element of dynamical certainty must enter. The address as a whole is an eloquent and pleasing presentation of a fundamental question in natural philosophy.

W. F. M.

Principles of Electrical Measurements. By Arthur Whitmore Smith. New York: McGraw-Hill Book Company, 1914. Pp. xiv+233. Price, $2.00 net.

This book is designed for beginners in electrical engineering or for advanced students in physics who wish to master the details of electrical measurements. The book is self-contained in that, before any set of experiments is described, the elementary facts, the definitions and laws are presented which are necessary to an understanding of the experiments. There is not the same preparation made for the understanding of the instruments which are used in the experiments. They are apparently to be taken on faith. All the usual problems of electrical measurements are adequately discussed. The treatment of magnetism is particularly developed. It appears that the subject is one which has been of special interest to the author.

W. F. M.

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PHYSICAL REVIEW.

A METHOD OF DETERMINING THE RADIANT LUMINOUS EFFICIENCY OF A LIGHT SOURCE BY MEANS OF A CELL WHOSE TRANSMISSION CURVE IS IDENTICAL WITH THE LUMINOSITY CURVE OF THE AVERAGE EYE.[1]

BY ENOCH KARRER.

CONTENTS.

CONSIDERABLE work has been done upon the subject included in the above title, under the names of "luminous efficiency" and "radiant efficiency." Very little of it, however, can have any bearing upon or connection with other photometric quantities, because in most instances no account was taken of the fact that all radiation in the visible spectrum is not equally powerful in producing light.

By the radiant luminous efficiency of any source is meant the ratio of the energy of the radiation emitted *weighted in accordance with its effectiveness* in producing the sensation of light, to the energy of the total radiation emitted.[2] This may be indicated thus:

$$\text{Radiant Luminous Efficiency} = \mu_R = \int_0^\infty \frac{E_\lambda(V_\lambda)d\lambda}{E_\lambda d\lambda},$$

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[1] Abstract of this paper was read before the New York meeting of Physical Society October 31, 1914.

[2] For the definition of this quantity in relation to other suggested definitions of photometric quantities see H. E. Ives, Lighting Journal, Oct., 1913.

where V_λ is the visibility of wave-length λ obtained from the equal energy luminosity curve[1] of the normal eye; and $E_\lambda d\lambda$ is the energy at wave-length λ.

To see clearly what is meant by the luminosity mentioned above we may proceed as follows: Suppose we have a spectrum of a carbon filament lamp. If now we take from the region of wave-length .55 μ a certain amount of energy measured with a thermo-couple, say, and compare its brightness with the light of a candle, we will find a certain number representing its intensity, say one. Now, if energy is taken from some other region, say near wave-length .61 μ, we will find that for the same amount of energy we get approximately one half the candle power, or the number 0.5 representing its intensity. Thus we might go through the spectrum and determine the "light-value" of a definite and constant amount of energy at the various wave-lengths.

The equal energy luminosity of the observer's eye, then, is obtained by plotting the values determined above against the corresponding wave-lengths. This has been done by Ives[1] for many eyes; and a curve for the "average eye" has been obtained. This has a very important bearing upon many determinations and problems in photometry; and it is readily seen that the determination of luminous efficiencies made by merely selecting a certain region in the spectrum, from .4 μ to .72 μ as has been commonly done, without regard to the manner in which this radiation affects the eye, can have no accurate meaning in practice.

The object of the present research was to develop a method of measuring radiant luminous efficiencies according to the above considerations.

There are several possible modes of obtaining the quantity defined as the radiant luminous efficiency.

First. An energy curve of the source in question may be plotted, The ordinates of this curve represent the energy of the radiation at various wave-lengths (abscissæ). Now, if these ordinates be multiplied by the ordinates of the luminosity curve, representing the weight to be given each wave-length in producing light, we obtain numbers which will represent the light produced by each wave-length. A curve then may be drawn with these numbers as ordinates and wave-lengths as abscissæ. The area of this latter curve is proportional to the energy of the radiation properly rated as to its "light-value." The area included by the original energy curve measures the total energy of the radiation. The ratio of the former area to the latter gives μ.

Langley[2] and others have employed graphical methods for obtaining ratios of radiation weighted in different ways.

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[1] Ives, Phil. Mag., Dec., 1912.

[2] Sci., June 1, 1883; Phil. Mag., May 30, 260, 1890.

Second. A screen with an aperture of suitable form may be used. This will be made clear by the following considerations:

Suppose we had a spectrum which had equal quantities of energy in the regions of every wave-length, and consider the radiation that passes through an aperture of the shape of the luminosity curve. The energy at each wave-length will be proportional to its light-giving power.

If, now, the spectrum of any source in question is formed with the same dispersing apparatus and allowed to pass through a screen with this aperture, the radiation from the source will be properly rated. We measure the energy in the spectrum after passing through the screen, and also the total energy without the screen. The ratio of the former to the latter is the radiant luminous efficiency sought. In unpublished work this method was suggested by Dr. Pfund in 1906; and also by Strache[1] in 1911.

Third. An absorbing solution may be made whose transmission curve is identical with the luminosity curve. Houstoun[2] has suggested the method. This is the method fully developed and described in this paper.[3]

Fourth.[4] Ives[5] has suggested the possibility of finding a photoelectric cell properly screened whose sensibility for various wave-lengths is of appropriate relative magnitude. Coblentz[3] suggests the possibility of finding a photoelectric radiometer with a sensibility curve that of the eye.

Fifth. A calorimetric method. This is described by Nichols[4] and it is not essential to describe it here. The purpose of the present investigation was to construct a cell with suitable absorbing solutions to be used in the direct determination of luminous efficiency. The transmission of such a cell must be such as to allow quantities of the radiation of any wave-length to pass through proportional to the luminosity of that wave-length; that is, the transmission curve must be identical with the luminosity curve of the average eye as given by Ives. The thermocouple screened with this cell in series with the galvanometer will respond to the radiation proportional to the true light value, that is, as the eye responds to that radiation giving the sensation of light.

The investigation is divided into two parts:

Part 1. An investigation of the transmission solutions contained in a quartz cell. The general method is obviously to measure the incident

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[1] Proc. Amer. Gas Inst., 2, 401, 1911.

[2] Proc. Roy. Soc., 85 (A), 275, 1911.

[3] Phil. Mag., p. 853, Dec., 1912.

[5] Nichols, Lab. Manual, Vol. II., p. 325.

[3] A photographic method might be suggested here, with proper plates or plate in conjunction with suitable screen.

[4] Bul. B. of S., Vol. 9, page 46, 1913.

and transmitted radiation; and for this purpose a thermocouple was used. The scheme of apparatus used in this part is shown in Fig. 1.

The current through the Nernst glower was maintained at 0.8 ampere by potential from a storage battery. The carbon arc was tried as a source for radiation in the violet, but was found entirely unsatisfactory due to unsteadiness. The Nernst glower was used throughout the investigation of the transmission of solutions. The glower was protected from air currents by a small wooden box lined with heavy asbestos, which was just sufficiently large to receive the metal casing in which the filament was mounted. The box has a brass door with an aperture to allow full illumination of the first lens surface.

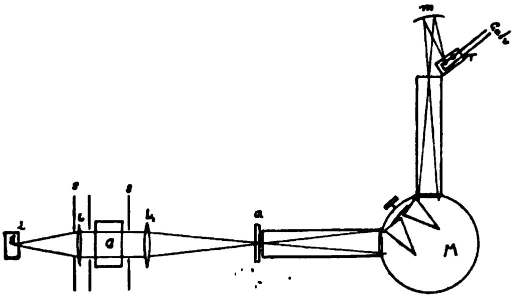

Fig. 1.
g = Nernst glower in inclosure *i*.
l, l_1, lenses.
s, s_1, screens.
c, cell containing solutions to be investigated.
a, auxiliary cell.
M, monochromatic illuminator.
m, silver concave mirror.
T, thermo-element.

The lenses *l*, l_1 had a focal length of 14.5 cm. and diameter of 4 cm. Screen *s* was of heavy cardboard with a circular aperture of diameter somewhat less than 4 cm. so that the side walls of the cell (*c*) were not illuminated.

The cell (*a*) contained clear distilled water or a concentrated solution of copper chloride; the former when the longer wave-lengths were used, the latter when short wave-lengths were used. This auxiliary screen was placed as near as possible to the receiving slit of the illumination. It was designed to avoid the vitiating effects of scattered radiation.

The monochromatic illuminator was calibrated by means of the following lines: potassium 7,682, lithium 6,708, sodium 5,893, mercury (arc) 5,780, 5,461, 4,916, 4,358, 4,078. This calibration was checked several times during the work to detect any instrumental shifts. The light from the transmitting slit was focused upon the thermocouple (*T*) by means of a short-focus concave silvered mirror (*m*). This was kept well polished always.

The thermocouple used in this part of the work was one constructed by Dr. Pfund[1] and used by him in measuring stellar radiation.[2] The thermo-element was enclosed in a sealed tube with a fluorite window. Evacuation was accomplished by means of Pfund's charcoal evacuator.[3] The degree of exhaustion was tested several times during the progress of the work and no diminution was noted even after months of service. For a detailed description the reader is referred to the original papers.[3]

The thermo-element was fastened securely in a box. Short leads connected its terminals with two large copper plates, also securely fastened in the box. Two additional wires led from the copper plates backwards. The box was then entirely filled with fine sand, to protect the thermo-element from convection currents. The copper plates were designed to act as heat reservoirs, so that conduction of heat energy to the thermal-element through the external leads would have little effect upon the galvanometer system. Over this box—with a suitable aperture to receive the light—was placed another box lined with heavy paper.

The galvanometer used in conjunction with the thermo-element was of a D'Arsonval type and was constructed by Dr. Pfund. It was designed to be quite stable and have sensibility sufficient for the present purpose. The suspension was of silver and about 10 cm. long. It was provided with a concave mirror approximately 2.5 × 3.5 mm. and of long focal length. Its period on open circuit was 15 sec. The galvanometer was enclosed in a box mounted upon an outside brick wall. The box was loosely packed with cotton. The mirror was seen through an aperture in the front of the box. This was covered with a thin strip of glass during the greater part of the work. The scale mounted upon ground-glass was four meters from the galvanometer and was supported upon a bracket securely fixed to a brick wall also. The image of a filament of an incandescent lamp was formed upon the ground-glass. The deflections were read with a hand glass magnifying about two and one half times. Later in the work advantage was taken of the diffraction images formed by the small mirror. With the reading lens the maxima and minima were very sharp and very easily seen.[4] The first dark space was about

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[1] Phys. Zeit., 13, 870, 1912; Phys. Rev., XXXIV., 228, 1912.

[2] Pub. Allegheny Observatory, III., No. 6, p. 43.

[3] Phys. Zeit., 13, 870, 1912.

[4] Many maxima and minima could be seen sharply defined on either side of the central bright image.

the width of the lines on the scale. This first dark space was used instead of the bright central image. This proved to be a very convenient and accurate method of reading the deflections. The method was first suggested and tried by Dr. Pfund. A sliding holder for the lens was constructed so that the diffraction image could be followed more comfortably as the mirror deflected. A little scale rider graduated to tenths of millimeters was made. This could be pushed along with the lens to aid in estimating fractions of a millimeter. For the most part tenths of millimeters were estimated without the aid of the rider. The galvanometer system was remarkably free from accidental disturbances. There was very little drift of the zero point except owing to the extreme variations in the room temperature from morning to night. During the latter part of the work the space between the scale and the galvanometer was enclosed by means of tin pipe to avoid the scintillation of the image due to convection currents in the air. The galvanometer with the thermo-element in series with it was just critically damped. This condition was accurately brought about by adjusting an iron bar across the poles of the field magnet. The sensibility of the galvanometer and thermo-couple was such as to give 26 cm. deflection when a candle was placed at a distance of 1 meter in front of the thermo-element.

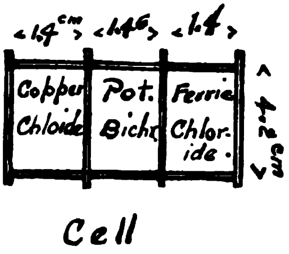

Fig. 2.

The deflections of the galvanometer were accurately proportional to the energy falling upon the thermocouple. This had been established by Dr. Pfund in a long series of tests made in the course of previous work.

The cell which contained the solutions investigated had three compartments as shown in Fig. 2. It was made from three rings cut from ink bottles. The rings were ground to have approximately parallel edges. They were cemented, by means of Canada balsam, end-on with quartz plates between and at both ends. The plates between the rings were 42 × 42 × 1 mm. while those at the ends were circular 42 mm. in diameter and 2 mm. thick. An opening was cut into each ring for purposes of filling. The quartz plates were purchased from The John A. Brashear Co. and the Bausch & Lomb Optical Co. They were only approximately plane parallel, but they were so placed on the rings that their individual defects were largely neutralized. The quartz plates were adjusted also so that the completed cell had quite perfectly parallel surfaces. This was tested by inserting the cell filled with water in front of a telescope focused on a distant church steeple. There was some prismatic effect in the vertical plane; but this was not objectionable since it would cause a displacement of the image of the Nernst filament lengthwise along the slit of the monochromatic illuminator. When only one or two solutions were investigated the other compartment was filled with water. All the data given below were obtained with this cell. Other cells had been constructed and tried. They were made of plane parallel glass, but slight selective absorption of wave-lengths between .56 μ and .59 μ was noticed. On this account the cells were discarded. Quartz, on the other hand, offers a great advantage in that it can be readily duplicated.

The method of making determinations was as follows:

The solutions were put into the cell; the graduated head of the illuminator set to give the desired wave-length; the thermoelement was exposed to this wave-length first when the above cell was in the optical path and, second, when it was out; the ratio of the deflection in the first case to the deflection in the second case gives the percentage of transmission.

Determinations of this kind were made throughout the visible spectrum at intervals of .01 μ. These percentages of absorption were plotted against wave-lengths, that at .55 μ being taken as unity because this is the wave-length of maximum luminosity. This curve could then be compared with the luminosity curve[1] plotted to the same scale. To obtain a rough idea of the transmission curve of any set of solutions readings were made at .55 μ, .51 μ, .48 μ, .60 μ and .64 μ. This was sufficient to show what must be done to the solutions to approximate the luminosity curve, or whether they were suitable at all.

The slits used were as small as possible and still allow deflections accurately readable. In the extreme blue the widths were approximately 0.4 to 0.6 mm.; in the longer wave-lengths much less—in the red less than 0.1 mm.; at wave-length of maximum luminosity the slit width was approximately 0.2 mm. No corrections were applied for slit width.

There was always present a slight amount of stray light, through the monochromatic illuminator. In the final cell, however, with its high transmission, this was comparatively small. In the extreme blue, where large slits had to be used, another method was adopted as a check. A thin glass cell was made, filled with concentrated potassium bichromate solution. This was inserted immediately in front of the first slit of the illuminator. The opaque screen was raised; and, when the galvanometer became steady, the little cell was suddenly removed. The additional deflection was noted. This was entirely due to the blue at which the

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[1] H. E. Ives, "Spectral Luminosity Curve of the Average Eye," Phil. Mag., Dec., 1912.

illuminator was set and which was out when the bichromate screen was in place. To avoid any displacement of the image of the Nernst filament and change in focus when the bichromate screen was taken out and replaced, the latter was immersed in a water cell which was always in front of the slit. The optical path was thus kept practically constant.

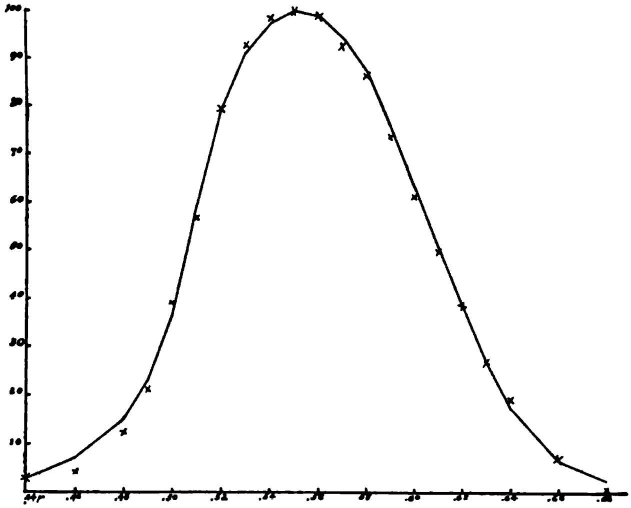

Fig. 3.

Transmission curve of cell in crosses Luminosity curve in full line.

It was found that the shifting of the zero noticed at the beginning of a series of observations could be eliminated quite completely by opening the slits and exposing the thermocouple for several minutes to the radiation from the Nernst glower. After this exposure the zero would remain constant.

Many inorganic salts were investigated; but only a few organic ones. Over two dozen dyes were examined in various combinations. The common difficulties with the dyes are that their absorption is high; they have sharp bands; and usually those having the adequate absorption near .60–.64 μ become again transparent in the infra-red. An additional objection is their instability and the uncertainty of exactly reproducing them.

The solutions that were found to answer requirements most satisfactorily with the cell above described were:

1. Cupric chloride ($CuCl_2 + 2H_2O$) purchased from Eimer & Amend. Analysis showing some trace of iron (0.0025 per cent.) and of sulphur (0.0016 per cent.) 41.085 grams of the salt were dissolved in one litre of distilled water. This solution was contained in the first compartment of cell 1.4 cm. in thickness.

2. Potassium bichromate ($K_2Cr_2O_7$, M. W. 294.5) purchased from J. T. Baker & Co., N. J. Analysis showing traces of calcium (0.001 per cent.) and of chloride (0.0001 per cent.) and sulphite (0.01 per cent.) 0.83462 gram per liter. This was contained in the middle compartment of the cell 1.46 cm. thick.

3. Ferric chloride (Fe Cl_3, $6H_2O$; M. W. 270.32) purchased from J. T. Baker & Co., N. J. Showing by analsyis P—trace, SO_3 0.002 per cent., HNO_3—trace, As—trace. 5.8712 grams per liter. Contained in the third compartment of the cell 1.4 cm. thick.

The concentrations of these solutions given above for thickness actually used become for a thickness of 1 cm. as follows:

Cupric chloride	57.5190 gm./l.
Potassium bichromate	1.2190 "
Ferric chloride	8.2200 "

The values for the transmission could be duplicated to within one per cent. on the red side of the maximum and to within four or five per cent. on the blue side. After four or five days the ferric chloride solution becomes opaque. Throughout the measurements made here this solution was prepared anew every other day. A certain percentage solution of iodine and potassium iodide can be substituted for the ferric chloride solution. This solution is .0515 gm. iodine with .4047 gm. potassium iodide to one liter of water. This iodine solution was used several days after preparation. It was contained however in a sealed jar. Whether there is any preponderating advantage to substitute it for the iron solution used cannot be stated at this time.

The values given in Table I. for the transmission are for the most part the means of four sets of data taken when the cell had been filled anew with new solutions. In each set three or four readings were taken at each wave-length. The measurements were taken at room temperature (about 19° C.). The temperature coefficient is too small to cause any noticeable change in absorption for a variation of a few degrees. The variations from the mean are less than 5 per cent. with the exception of three readings at 52, 54 and 55; considerably less in most cases, particularly on the red side of the maximum.

The deflections obtained without the cell were: At .50 μ 27.7 mm.; at .55 μ 39 mm.; at .60 μ 29 mm.; at .64 μ 45 mm.

Table I. shows the absolute transmission T in per cent. and the relative transmission T_r. Under V are given the corresponding values of the luminosity.[1] In column 1 are the wave-lengths; in column 2, the percentage transmission; in column 3, relative transmission, with that at .55 μ taken as 100; in column 4, the corresponding values for the

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[1] Ives, Phil. Mag., Dec., 1912, p. 859.

TABLE I.

λ	T	T_r	V
.44μ		2.0	2.9
.46		4.0	7.3
.48	7.4	12.3	15.4
.49	12.8	21.3	23.5
.50	23.6	39.2	36.3
.51	34.2	57.0	59.6
.52	47.6	79.3	79.4
.53	55.9	93.0	91.2
.54	59.1	98.5	97.7
.55	60.0	100.0	100.0
.56	59.6	99.2	99.0
.57	55.4	92.5	94.8
.58	51.9	86.5	87.5
.59	44.4	73.8	76.3
.60	37.1	61.5	63.5
.61	30.0	50.0	50.9
.62	33.3	38.7	38.7
.63	16.3	27.1	27.2
.64	11.7	19.5	17.5
.65	4.3	7.1	6.8
.68	1.0	1.7	2.6

luminosity taken from Ives.[1] Below .48 μ and above .68 μ the curve is extended, for no readings here were taken. At .70 μ there was practically zero transmission; beyond .70 μ there was also zero transmission. The amount of energy given by the Nernst glower in wave-lengths below .48 μ is so small that a very large slit must be used and the measurements are very inaccurate. The transmission, however, extends down to .43 μ as is shown by the fact that the line of the mercury arc at .43 μ can be plainly see through the cell.

In Fig. 3 are given the transmission curve in crosses, and the luminosity curve of the average eye as found by Ives in full line. By means of a planimeter the areas of these curves were obtained. The area of the transmission curve is about 2.9 per cent. smaller than that of the luminosity one. It will be observed, however, that it is in the extreme blue where the maximum difference between the curves exists. In this region most light sources are deficient, so that the errors committed by using the cell is certainly much less than this.

The value of a knowledge of the radiant luminous efficiency of a light source may not be obvious to the reader who is not engaged in photometry, or who is not a worker in the profession of the lighting engineer. This quantity gives us a very interesting and valuable characteristic of

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[1] Ives, Phil. Mag., Dec., 1912, p. 859.

the light source. It has close associations obviously with the total luminous efficiency, *i. e.*, the ratio of the radiations rated according to their luminosity to the total energy-input into the light source. For, knowing the losses (*e. g.*, in the case of the filament lamp, losses due to convection, conduction and resistance of the lead-in wires) the total luminous efficiency may be found from the radiant luminous efficiency.

Knowing the radiant luminous efficiency we would also know the total luminous efficiency from another consideration. For if we knew the watt equivalent of unit flux density of light of any wave-length we can also readily find the total luminous efficiency. The quantity to which reference has just been made has been termed the mechanical equivalent[1] of light. In our calculations we must take the "mechanical equivalent" of the radiation at wave-length of maximum luminosity (550 $\mu\mu$).

Calling the lumens per watt or radiation of wave-length 550 $\mu\mu$, $K_{\max}$, we have

$$\frac{1}{K_{\max}} = \text{watts per lumen}$$

or

$$\frac{4\pi}{K_{\max}} = \text{watts per mean spherical candle.}$$

The radiant luminous efficiency (μ_R) tells us that only μ_R per cent. of the total radiation is light when the radiation is properly valued. Therefore,

$$\frac{4\pi}{K_{\max}} \div \mu_R = \text{watts per mean spherical candle.}$$

Again, to fully and definitely describe a light source this quantity must be known. This will be seen by the following considerations. We may have two light sources which have the same value for the total luminous efficiency, *i. e.*, they may have the same energy-input and give the same amount of light radiation. Yet they may have quite different values of radiant luminous efficiency. The total luminous efficiency gives us the quantity which is most important from the economic standpoint; but is not by any means the only characteristic which we wish to know and must know for further development of our light sources.

In order that this quantity may mean what it should, however, all effects of radiation from mechanical parts connected with the source must be eliminated. The energy radiated only from the primary incandescent or luminous parts must be considered. This means that correc-

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[1] Since the above work has been done Dr. Ives, Dr. Coblentz and Mr. Kingsbury have made an accurate determination of this quantity.

tion must be made for radiation from the chimney, from the bulb or other enclosure, and from the envelope of hot gases in case of certain sources. For this reason great accuracy for the values given below cannot be claimed. Correction was made only for one of the sources studied. The full significance of what errors due to this cause may be was fully realized in case of the mercury arc. Possibly to the illuminating engineer it is of greater usefulness to know the radiant luminous efficiency of the light source as it is used, that is without the corrections above applied.

It is obvious that the radiation measurements are not measurements involving in actual procedure the whole of the energy of radiation from the source; a particular direction and a particular solid angle are chosen. The direction is such as is usually of greatest interest for other measurements of the light sources studied.

Strictly in accordance with definition the whole energy of radiation in each case should be considered. The values obtained for the radiant luminous efficiency may be quite different in different directions. This must be so in case of the carbon arc and mercury arc and acetylene burner.[1] This has not been investigated and the author is not aware that any work or statement has been made upon this point. We might define other quantities such as the mean horizontal and the mean spherical value of the radiant luminous efficiency to be in correspondence with the measurements of candle power.

Part II. With this cell it was purposed to determine the radiant luminous efficiency of various light sources. This has only in part been accomplished; a few of the many sources have been studied, and all necessary corrections perhaps have not been applied.

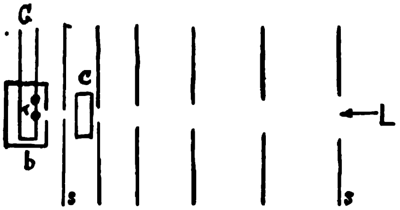

Fig. 4.

T, thermo-element with enclosure *b*.
s . . . *s*, screens.
g, galvanometer.
l, light source investigated.
C, cell.

The general arrangement of the apparatus for this portion of the work is shown in Fig. 4 above.

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[1] Bul. Bur. Stand., Vol. 7, 1911.

This portion of the work was carried out, in most part, in the research laboratory of the United Gas Improvement Co. of Philadelphia, where access was had to various standard sources authoritatively rated. The new type of Leeds & Northrup galvanometer was used. The scale and telescope were at a distance of two meters from the galvanometer. This was made possible by placing immediately in front of the galvanometer a spherical concave spectacle lens (.25). Tenths of millimeters could easily be estimated for the image of the scale was almost natural size.

A Ruben's thermopile was used. This was employed instead of Pfund's thermocouple to avoid the uncertainty of absorption by the fluorite window for the various light sources.

About 22 cm. deflections were obtained with a candle at the distance of a meter. There was a very great lag, however, and a steady drift of the zero. Though the critical damping resistance of the galvanometer was 32 ohms this damping was not present when much greater resistance was inserted. To overcome this and the uncertainty as to what the effective distance was with a metallic cone before the junctions, the thermopile was dismantled of all its metal parts and mounted on a block of wood enclosed in a small pasteboard box with suitable aperture. Fine short leads connected it to two large pieces of brass cylinder; from which in turn two fine leads extended outwards. This box was loosely packed with cotton and enclosed in a second larger box mounted upon a long photometer bench constructed for the purpose. This last was also packed with cotton. There was now much less lagging and drift, though a considerable loss of sensibility was sacrificed. A series of screens was made of heavy cardboard mounted upon suitable blocks to fit the photometer bars. These screens had apertures of gradually decreasing size. They were stationed at intervals of from 10 to 20 cm. along the bar between the light source and the thermocouple.

The cell was mounted upon a small frame for which an appropriate sliding space with stops was arranged, so that the cell would be pushed aside and replaced in exactly the same position. The cell was placed as near as possible to the thermopile. Accurately round apertures in a thin board were painted black and placed immediately before and behind the cell. These apertures were a trifle smaller in diameter than the cell, to prevent any reflected light not going through the cell from reaching the thermopile.

The angle subtended by the thermopile at a distance of 63 cm. was one whose cross-section was 4 cm. horizontally by 22 cm. vertically. This angle was sufficiently large to include the whole surface of most of the illuminants investigated

The galvanometer deflections in the ranges occurring throughout the experiment were proportional to the energy falling upon the thermocouple. This was borne out for some very large deflections where the deviation was well under one per cent. The time required to reach a maximum deflection was approximately twenty-five seconds.

To take a set of measurements the light source was moved to a convenient distance; the thermoelement was exposed by raising a screen of heavy card suitably connected to a system of pulleys easily operated by the observer at the telescope; the maximum deflection was noted (the zero before and after being also noted); the cell was now pushed into position; the light source was moved sufficiently nearer, and a similar set of readings taken; the cell was then removed; the light source moved out to its first position and readings repeated. From ten to twenty readings were taken for each setting. For most of the sources recorded a similar series was taken on the two different days. There was always some drifting of the zero; and, though the galvanometer was mounted in the basement on the stone wall, accidental deflections due to mechanical disturbances from the mechanic's shop on the first floor were often considerable. The galvanometer suspension was very short,

TABLE II.

Welsbach Mantle Ceria 2 Per Cent. with Cell.

Zero.		D	r_v
Before.	After.		
2.30	2.10	3.70	1.50
2.10	2.10	3.65	1.55
2.10	2.10	3.80	1.70
2.10	2.13	3.75	1.64
2.13	2.25	3.86	1.67
2.25	2.35	3.97	1.67
2.35	2.50	4.11	1.69
2.65	2.80	4.45	1.73
2.80	2.90	4.60	1.75
2.90	3.05	4.55	1.58
2.42	2.60	4.16	1.65
2.60	2.62	4.25	1.64
2.62	2.70	4.32	1.66
2.70	2.78	4.15	1.41
2.78	2.90	4.55	1.71
2.90	3.00	4.56	1.61
3.00	3.05	4.70	1.68
3.05	3.20	4.75	1.63
			Mean 1.63

which made such effects much more pronounced. The errors resulting from these sources were reduced by the large number of observations made.

Results.—A series of typical readings for the Welsbach mantle (2 per cent. ceria) with the cell is given in Table II.; for the same without the cell in Table III.; for the carbon point source (4*w*/*c*) readings with and without the cell are given in Table IV., and Table V. respectively; for the new tungsten-nitrogen filled lamp (.65 *w*/*c*) in Tables VI. and VII. respectively.

TABLE III.

Mantle 2 Per Cent. Ceria. Without Cell.

Zero.		D	r_t
Before.	After.		
2.15	2.10	24.46	22.34
2.10	2.32	24.82	22.61
2.32	2.40	24.95	22.59
2.40	2.25	24.96	22.62
2.25	2.08	24.90	22.74
2.08	1.85	24.75	22.79
1.85	1.82	24.60	22.77
1.82	1.70	24.49	22.73
1.70	1.58	24.47	22.83
1.58	1.40	24.30	22.81
1.40	1.38	24.20	22.81
1.10	0.93	23.70	22.69
0.93	0.80	23.75	22.92
0.80	0.43	23.55	22.91
2.35	1.95	25.50	23.35
1.80	1.55	24.47	22.80
1.55	1.30	24.40	22.98
1.20	0.95	24.12	23.05
0.95	1.10	23.98	22.96
1.10	0.95	24.05	23.03
0.67	1.10	24.45	23.57
1.00	1.00	24.25	23.25
0.85	0.70	24.15	23.43
0.40	0.20	23.80	23.50

In columns one and two of each table are given the positions of the zero point before and after deflection; in column three, the observed maximum deflection; in column four, the true maximum deflections (r); (*i. e.*, column three corrected for position of "zero" as given by columns one and two).

In Table VIII. the means for all the sources studied are given, together with the corresponding distances and the ratio μ defined as the radiant

Table IV.

Carbon 99 v. (4 w/c). With Cell.

Zero.		D	r_v
Before.	**After.**		
2.47	2.50	4.75	2.27
2.50	2.48	4.78	2.29
2.48	2.48	4.70	2.22
2.48	2.57	4.80	2.28
2.57	2.55	4.81	2.25
2.55	2.58	4.82	2.26
2.58	2.64	4.90	2.29
2.64	2.70	4.99	2.32
2.70	2.72	5.00	2.29
2.72	2.80	5.01	2.25
2.80	2.87	5.17	2.34
2.87	3.00	5.24	2.31
3.00	3.05	5.37	2.35
3.00	3.08	5.33	2.29
3.08	3.13	5.40	2.30
3.13	3.15	5.43	2.29
3.15	3.20	5.48	2.31
3.20	3.30	5.58	2.33
3.30	3.40	5.63	2.28
3.40	3.40	5.70	2.30
			Mean 2.28

luminous efficiency. In column one are given the deflections (r_v) with the cell in place and with the source at a distance (d_v) as given in column three; corresponding quantities r_t and d_t without the cell are given in columns two and four. In column five is given the efficiency for each source.

The distances d_v are corrected for the change in optical distance due to the glass and water of the cell. This amounts to 0.7 mm. and was subtracted from the distances measured. All distances and deflections are given in centimeters.

μ has been defined as above as

$$\frac{\text{Radiated energy} \times \text{luminosity}}{\text{total radiated energy}}.$$

With a cell whose transmission is identical with the luminosity curve this becomes

$$\frac{\text{Radiated energy} \times \text{transmission}}{\text{total radiated energy}}.$$

$$\mu = \frac{\int E_\lambda V_\lambda d\lambda}{\int E_\lambda d\lambda} = \frac{\int E_\lambda A_\lambda d\lambda}{\int E_\lambda d\lambda},$$

where A_λ is the absorption by the cell at wave-length λ.

Table V.

Carbon 4 w/c 99 v. Without Cell.

Zero.		D	r_t
Before.	After.		
0.00	−0.12	50.30	50.36
−0.12	−0.28	50.36	50.56
−0.28	−0.62	50.33	50.78
−0.62	−0.60	50.20	50.81
−0.60	−0.60	50.50	51.10
−0.60	−0.30	50.48	59.93
−0.30	−0.60	50.32	50.77
−0.60	−0.65	50.12	50.74
−0.65	−0.80	50.30	51.02
−0.80	−0.50	50.21	50.86
−0.50	−0.88	50.28	50.97
−0.88	−0.78	50.45	51.25
−0.78	−0.75	50.10	50.86
−0.75	−0.53	50.22	50.86
−0.53	−0.60	50.25	50.82
−0.60	−0.62	50.50	51.11
−0.67	−0.62	50.40	51.04
−0.62	−1.20	50.13	51.04
−1.20	−0.72	50.20	51.16
−0.72	−0.70	50.12	50.83
−0.70	−1.40	50.80	51.85
			Mean 50.93

In Table VIII. above r_v is a measure of the energy after going through the cell and r_t is a measure of the total radiation, but to make these comparable they must be corrected. First, for distance. The deflections r_v and r_t must be reduced to the values they would have had if the source had been at some fixed distance for both (unit distance, say). That is, r_v must be multiplied by d_v^2 and r_t by d_t^2. Second, with the cell in, all of the radiation at any wave-length does not have effect upon the thermo-couple for a certain amount is absorbed by the cell. Experiments made with radiation of wave-length .55 μ proved that only 60 per cent. of the energy at that wave-length is transmitted; hence, r_v must be multiplied by 100/60. Therefore

$$\mu = \frac{100\dfrac{r_v \times d_v^2}{60}}{r_t \times d_t^2}.$$

The values of μ given in column five are calculated from this equation for each source.

The radiation from the whole lamp was in each case allowed to fall

TABLE VI.

Tungsten (.65 w/c) 6.6 amp. With Cell.

Zero.		D	r_e
Before.	After.		
7.02	7.10	14.02	6.96
7.10	7.20	14.00	6.85
7.20	7.28	14.12	6.88
7.28	7.26	14.20	6.92
7.26	7.40	14.20	6.87
7.40	7.40	14.30	6.90
7.40	7.45	14.34	6.92
7.45	7.40	14.30	6.88
7.40	7.49	14.28	6.84
7.49	7.60	14.57	7.03
7.60	7.63	14.53	6.92
7.63	7.75	14.63	6.94
7.68	7.75	14.55	6.84
7.75	7.80	14.75	6.98
7.80	7.85	14.52	6.70
7.85	7.80	14.70	6.88
7.80	7.85	14.70	6.88
7.85	7.90	14.76	6.89
7.90	7.89	14.70	6.81
7.89	7.88	14.90	7.02
7.88	8.00	14.85	6.91
8.00	7.95	14.95	6.98

upon the thermopile. No correction was made for the radiation from any portion of the mechanism, which is an essential part of the light source as ordinarily used. For example, no correction was made for the radiation from the chimney of the Welsbach mantle lamp. For an accurate determination of the efficiency of the mantle itself such a correction must be made, by getting a cooling curve of the chimney.[1] Such a correction would increase the efficiencies recorded above. The incandescent electric lamps used were matched in color on the photometer by Mr. Kingsbury of the photometrical laboratory of the U. G. I. Co. against standards of approved type prepared by the Electrical Testing Laboratories, New York City.

The values for the tungsten lamps are inversely proportional to the watts per candle ratings. This is to be expected since the losses in incandescent lamps are proportional very approximately to the watts per candle.

A similar calculation based upon watts per candle for the new tungsten and for the carbon filament lamps, taking the efficiency of the tungsten

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[1] Nichols, Laboratory Manual, Vol. II., p. 335.

Table VII.

Mazda (.65 w/c) 6.6 amp. Without Cell.

Zero.		D	r_t
Before.	After.		
9.20	8.98	35.70	26.62
8.97	9.75	36.25	26.89
9.75	9.25	35.80	26.30
9.25	8.60	35.80	26.38
8.60	8.75	35.15	26.48
8.75	8.65	35.65	26.95
8.65	8.55	35.40	26.80
8.55	9.30	35.75	26.33
9.30	8.60	35.90	26.95
8.60	8.65	35.15	26.53
8.65	9.22	35.60	26.67
9.22	9.20	36.12	26.91
9.20	9.00	35.20	26.10
8.88	8.95	35.45	26.54
8.95	10.00	36.20	26.73
10.00	9.45	36.45	26.73
9.53	8.85	36.05	26.86
8.85	7.80	35.05	26.73
7.80	8.15	34.96	26.99
8.15	7.45	34.60	26.80
7.80	7.72	34.48	26.67

(1.25 *w/c*) as 1.65, does not give the actual values observed. For the new tungsten lamp the value is 3.25, showing that the losses must be considerably more, or that the determined value of μ is too low, due to the excessive heating of the bulb. No correction was made for the hot gaseous envelope surrounding the candle and the open burner. The latter was a lava-tip burner consuming about four cubic feet of gas per hour. It had to be brought very close to the cell to get suitable deflections. At this distance the whole of the flame could not contribute to the deflection. Correcting the value of μ given above for this, the value becomes approximately 0.3 per cent. The mantle with 0.25 per cent. ceria is commercially known as "Iveslite" mantle. The one with 0.75 per cent. ceria is the mantle commonly used.

The chimney referred to above as "perforated" chimney had air rents around its base, in distinction from the solid chimney which had none. The gas was city gas of Philadelphia known as mixed gas rated at 650 B. T. U. per cu. ft. approximately; pressure 2.5 inches of water.

The mantle marked 1)*a* in the table consumed 3.8 cu. ft. per hour; 1)*b* 4.95 cu. ft. per hr.; 2) 3.6 cu. ft. per hr.; 3)*a* 4 cu. ft. per hr.; 3)*b* 5.2 cu. ft. per hr.

TABLE VIII.

Results for Various Sources.

Source.	r_v	r_t	d_v:	d_t	μ	Description.
Carbon filament	2.28	50.92	29.17	120.52	0.45	Point source 4 w/c 99v.
Nernst glower	4.65	28.46	20.39	102.90	1.08	0.8 amp. stereopticon type.
Tungsten-nitrogen	6.89	26.72	29.53	113.13	2.93	6.6 amp. (0.65 w/c)
Open burner	1.50	42.19	20.88	115.52	0.19	See below
Standard candle	0.25	8.67	16.45	73.85	0.24	Sperm candle
Mantles (1) *a*	0.89	21.34	44.8	163.3	0.5	0.25% Ceria
(1) *b*	1.48	23.57	44.9	163.4	0.7	0.25% Ceria
(2)	1.62	22.91	43.77	162.9	0.8	2% CeO_2
(3) *a*	2.90	21.43	37.60	163.4	1.2	Solid Chimney
b	3.81	26.91	37.6	163.4	1.26	perforated, 0.75% CeO_2
Tungsten (1)	3.65	16.28	27.75	119.47	1.99	102.6 v. 1 w/c
(2)	3.11	14.99	27.75	119.47	1.84	97.0 v. 1.1 w/c
(3)	2.51	13.53	27.75	119.47	1.65	9.16 v. 1.25 w/c
Mercury arc[1]	0.44	2.4	30.0	30.0	30.5	1.7 amp.

From 1)*a* and 1)*b* mantles it is seen that the efficiency varies with the gas consumption. This is to be expected for when an insufficient supply of gas is admitted, certain portions of the mantle will be cool; also when too much gas is admitted a small bunsen flame may exist above the mantle; both these conditions will lower the value of μ. The values for the mantles with varying per cent. of ceria are what might be expected from a study of the curves showing per cent. of ceria with candle power.[2] The mantle when used first indicated a greater efficiency than after a few hours burning, but was much more unsteady. Just how the radiant luminous efficiency changes for small changes in consumption at the point where the mantle is just filled and at its brightest would require more accurate measurements and steadier conditions. Two other determinations were made for the 4 *w/c* carbon lamp which make the mean value of μ equal to .43 per cent.

The Heraeus quartz arc at 10 amperes was also tried for efficiency. The quartz tube was between 6 and 8 cm. long and a portion of the tube only used. A screen of heavy cardboard with an aperture 2 cm. horizontally by 3 cm. vertically was placed immediately in front of the arc, in such a manner that it could be dropped and put in place only when deflections were taken. This was to insure that the screen itself would remain at room temperature. Values obtained for the arc are unsatisfactory. Taking measurements immediately after starting gave a value

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[1] Pfund's Type, PHYS. REV., N. S., Vol. III., No. 4, April, 1914.

[2] Johns Hopkins Lectures on Illuminating Engineering, M. C. Whittaker.

in μ in the neighborhood of 7 per cent. This value would steadily decrease for hours afterwards due to heating up of the tube.

Measurements were made in Baltimore with the new type of mercury arc recently described by Pfund.[1] The apparatus used was the same as that described in the first part of this paper. For Pfund's thermo-element as used, there was substituted the Ruben's thermopile as used in the measurements of the previous efficiencies. The procedure in this case was identical with the previous. The thermopile was carefully shielded and screens were placed at intervals between it and the source. The portion of the lamp just above the mass of mercury at the positive electrode was studied, the rest of the lamp being carefully screened off. This portion was 1.3 cm. wide by 1.8 cm. high. The lamp was placed 32 cm. from the thermopile and it was found unnecessary to move it. Even with the cell in place readable deflections were obtained. The current was 1.8 amp. taken from a storage battery with lamps in series as resistance.

Table IX. gives the zero position before and after in column 1; the position of maximum deflection, column 2; the magnitude of the deflections, column 3; both with the cell in place and without the cell.

To determine the correction to be applied due to the radiation from the walls of the tube, the lamp was put out and the time noted. Immediately thereafter the screen was drawn aside allowing the radiation from the dark hot tube to fall upon the thermopile. The deflection and the time were again noted. Several other deflections were obtained and times at which they were gotten were noted, while the tube cooled. These deflections and times reckoned in seconds are plotted in Fig. 5.

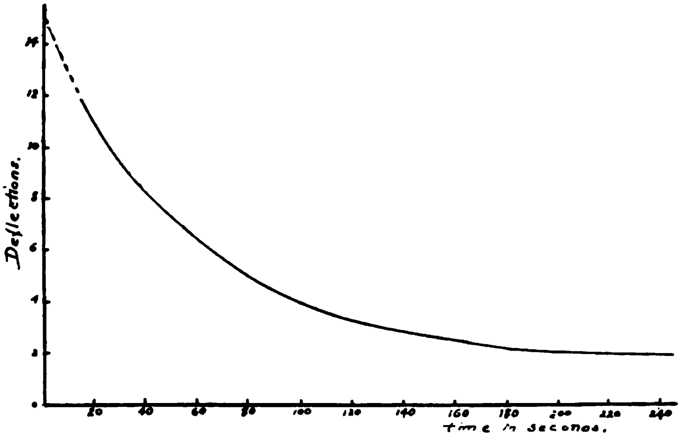

Fig. 5.

By exterpolation the deflection due to the radiation from the walls just at the time the lamp was quenched was obtained. This deflection was subtracted from the deflections recorded for total radiation. From the corrected deflections the value of the efficiency was then calculated. This is rather surprisingly high. This may be partly accounted for by the fact that the energy in the extreme violet and ultra-violet is not effective under this arrangement. Without correcting for the hot walls the value is only 4.2 per cent. This type of mercury arc, however, affords a very nice means of getting the radiant luminous efficiency through the quartz plate sealed to the upper end of the tube. By using a right-angled quartz prism much of the effect due to the heated tube could be at once eliminated. No such measurement was made at this time.

The carbon arc was found too unsteady to get reliable measurements. Magnetite electrodes were received from Dr. Whiteney, of the General Electric Laboratory, and various luminous carbons from Mr. Chillis, of the National Carbon Co. It is hoped that these will be studied in the near future.

TABLE IX.

Zero With Cell, Mm.	P_m, Cm.	Deflection, Cm.
0, −.3	.40	.41
0, −.3	.40	.41
0, 0	.43	.43
0, −.5	.42	.44
0, −.5	.43	.45
0, —.3	.45	.46
0, —0	.47	.47
0, −.2	.44	.45
0, —0	.45	.45
		Mean.........44
Without cell		
0, 1.1	17.7	17.2
0, .4	17.4	17.2
0, .5	17.4	17.2
0, .5	17.9	17.7
0, .2	17.4	17.3
0, .2	17.5	17.4
0, .4	17.9	17.7
0, .2	17.4	17.3
0, .2	17.6	17.5
		Mean......17.4

This work was suggested by Dr. H. E. Ives while the writer was working in the research laboratory of the United Gas Improvement Company of Philadelphia during the summer of 1913. To him the writer is greatly indebted for suggestions, for the standard illuminants used and for the many facilities placed at his disposal while measurements on efficiencies were made.

The writer wishes to express his appreciation of the interest of Professor Ames in this work and of the other members of the physics faculty, especially of Dr. Pfund, to whom grateful acknowledgment is made for suggestions and encouragement throughout the work.

Johns Hopkins University,
June, 1914.

THEORY AND USE OF THE MOLECULAR GAUGE.

By Saul Dushman.

SOME time ago Dr. I. Langmuir described the construction of a "molecular" gauge for the measurement of very small gas pressures.[1] At the suggestion of Dr. Langmuir the writer undertook a more detailed study of the theory and use of the instrument, and the following paper contains the results of a number of measurements that were carried out with the aid of this gauge.

Theoretical.

If a plane is moving in a given direction with velocity u relatively to another plane situated parallel to it at a distance d, there is exerted on the latter a dragging action whose magnitude may be calculated from considerations based on the kinetic theory of gases.

At comparatively higher pressures where the mean free path of the gas molecules is considerably smaller than the distance between the plates, the rate of transference of momentum across unit area is given by the equation

$$B = \frac{\eta u}{d}, \tag{1}$$

where η denotes the coefficient of viscosity.

According to the kinetic theory of gases this coefficient ought to be independent of the pressure. The confirmation of this deduction over a very large range of pressures has been looked upon as one of the most striking arguments for the validity of the assumptions on which the kinetic theory of gases is based.

It was found, however, by Kundt and Warburg,[2] that at very low pressures, where the mean free path of the molecules becomes of the same order of magnitude as the distance between a moving and stationary surface placed in the gas, there is distinct evidence of a slipping of gas molecules over the planes. The amount of this slip was found to be inversely proportional to the pressure.

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[1] Physical Review, *1*, 337 (1913). See also abstract, Phys. Rev., *2* (1913).

[2] Pogg. Ann., *155*, 340 (1875). Poynting and Thomson, Properties of Matter, p. 220.

Denoting the coefficient of slip by δ, it may be defined by the relation

$$v_g - v_s = \frac{\eta}{\zeta}\frac{\partial v}{\partial x} = \delta \cdot \frac{\partial v}{\partial x}, \tag{2}$$

where v_g = velocity of gas molecules at the surface,
v_s = velocity of surface,
ζ = coefficient of external viscosity.

It follows from hydrodynamical considerations that the amount of momentum transferred per unit area is

$$B = \frac{\eta u}{d + 2\delta}. \tag{3}$$

Thus, owing to slip there is an apparent increase in the thickness of the gas layer between the two surfaces. This increase amounts to $\delta = \eta/\zeta$ for each surface.

Experiments on the conduction of heat at low pressures led to similar observations in this case. According to the kinetic theory the heat conductivity should be independent of the pressure. Accurate determinations showed that at very low pressures the conductivity apparently decreases. This led to the conception that at the surface there occurs a very steep temperature gradient (Temperatursprung) so that the amount of heat, Q, conducted between two surfaces maintained at temperatures T_1 and T_2 is given by

$$Q = \frac{T_1 - T_2}{d + 2\gamma}, \tag{4}$$

where d is the distance between the two plates and γ represents the apparent increase in thickness of the layer of gas at each surface.

The definition of γ may be expressed by the following relation, which by its analogy with equation (2) helps to exhibit the complete parallelism of the phenomena observed in both the case of heat conduction and that of viscosity effect. Denoting the drop in temperature at the surface by ΔT, and the temperature gradient there by $\partial T/\partial x$, the definition of γ follows from the relation

$$\Delta T = \gamma \cdot \frac{\partial T}{\partial x}. \tag{5}$$

An interpretation of this temperature drop on the basis of the kinetic theory of gases was first advanced by Maxwell and subsequently developed still further by Smoluchowski.[1]

It is assumed that of the molecules striking a heated surface only a fraction f is absorbed and then emitted with an average kinetic energy

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[1] Ann. Phys., *35*, 983, where references to previous literature are given.

corresponding to that of the surface. The remainder $1 - f$ is reflected according to the laws of elastic collision. If T_1 denote the temperature of the molecules striking the surface, T_2, the temperature of the latter, and $T_2{}^1$ the temperature of the molecules leaving the surface, then:

$$T_2{}^1 - T_2 = (1 - f)(T_1 - T_2). \qquad (6)$$

The constant f is known as the coefficient of equalization (Smoluchowski) or accommodation (Knudsen),[1] for it is evident that f is unity when the average temperature of the molecules leaving the heated surface corresponds to the temperature of the latter.

In consequence of this lack of complete equalization of temperatures, there is produced an apparent temperature drop at the surface, which is related to the coefficient of equalization by the following equation:

$$\gamma = \frac{2 - f}{f} \cdot \frac{15}{4\pi} L, \qquad (7)$$

where L is the mean free path of the molecules at the given pressure.

The same method of interpretation was extended to the case of transference of momentum from one surface to another at very low gas pressures. Of the molecules striking a moving surface a portion β is "absorbed" and then "emitted" with velocities that range according to Maxwell's distribution law. The direction of emission is perfectly independent of the direction of incidence. On the other hand, the fraction $1 - \beta$ is "reflected" according to the laws of elastic collision.[2]

A number of investigators have concerned themselves with the mode of determination of these coefficients β and f, which may be designated as the coefficients of accommodation for viscosity and heat conduction respectively.

Knudsen,[3] who has carried out a large number of investigations on the behavior of gases at very low pressures, concludes that while the value of this coefficient is less than unity for heat conduction (and differs with the nature of the gas) it is equal to unity in all those cases where transference of momentum is concerned. He assumes, in other words, that all the molecules are emitted from a moving surface in directions which are absolutely independent of the original directions of incidence and that these molecules then obey Maxwell's law of distribution of velocities.

Timiriazeff[4] makes the assumption that the coefficient of accommodation has the same value, both for viscosity measurements and for the

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[1] Ann. Phys., *34*, 593 (1910).

[2] A. Timiriazeff, Ann. Phys., *40*, 978 (1913).

[3] Ann. Physik, *28*, 75 (1908); *31*, 205 (1909); *33*, 1435 (1910); *34*, 593, 823 (1911); *35*, 389 (1911); *36*, 871 (1911).

[4] *Ann. Physik*, *37*, 233 (1912).

determination of heat conduction in gases at low pressures and deduces from this assumption the relation

$$\delta = \frac{8}{15}\gamma \tag{8}$$

where δ has the significance assigned to it in equation (3) above.

From equations (7) and (8) it follows that

$$\delta = \frac{2}{\pi} \cdot \frac{2 - f}{f} \cdot L. \tag{9}$$

More generally, we can write

$$\delta = a \cdot L$$

where a is a constant whose exact value depends upon the particular assumptions made regarding the value of the accommodation coefficient.

At extremely low pressures, where L is large compared to d, equation (3) reduces to

$$B = \frac{\eta u}{2aL} \tag{10}$$

or, since

$$\frac{\eta}{L} = 0.31 p \sqrt{\frac{8M}{\pi RT}},$$

$$B = \frac{2 \times 0.31}{a} pu \sqrt{\frac{M}{2\pi RT}}. \tag{11}$$

Substituting for a the value deduced by Timiriazeff, see equation (9), it follows that

$$B = \frac{f}{2 - f} \times 0.31 \pi u p \sqrt{\frac{M}{2\pi RT}}. \tag{12}$$

A relation of the same form as this may also be deduced by means of considerations similar to those used by Knudsen. This method of derivation has the advantage that it does not involve any extrapolation of equation (3), but starts from fundamentally different premises.

At very low pressures, the mass of gas striking unit area of a surface per unit time is equal to

$$\frac{1}{4}\rho\Omega = p\sqrt{\frac{M}{2\pi RT}}$$

where

ρ = density of gas,

Ω = average (arithmetical) velocity.

Assuming, as Knudsen does, that the coefficient of accommodation is unity, it follows that the rate of transference of momentum per unit area from a surface moving with velocity u is

$$B = up\sqrt{\frac{M}{2\pi RT}}. \tag{13}$$

Equations (12) and (13) agree in the conclusion that at very low pressures B is proportional to $p\sqrt{M/RT}$.

According to Gaede,[1] Knudsen's assumption that the accommodation coefficient is equal to unity in the case of viscosity measurements at very low pressures is justified only at pressures below about 1.33 bars (.001 mm. of mercury). In a very recent paper, Baule has discussed the work of Smoluckowski, Knudsen, Timirazeff and others in detail[2] and by introducing some very plausible assumptions as to the actual mechanism by which a gas molecule exchanges energy with a molecule of the surface against which it strikes, he arrives at the relation

$$B = up\left(\frac{(1 - \alpha'\nu)}{(1 + \alpha'\nu)}\right)\sqrt{\frac{M}{2\pi RT}}, \tag{14}$$

where $\alpha'\nu$ is a function of the masses and diameters of the molecules of the gas and solid, and the distances between the molecules in the plane surface. It is thus evident that no two writers are agreed upon the manner in which the coefficient f is to be calculated.

We are, however, justified in concluding that there exists a relation between B and $p\sqrt{M/RT}$ of the general form

$$B = kup\sqrt{\frac{M}{RT}}, \tag{15}$$

where k is a *constant* whose value depends upon the nature of the gas and that of the surface with which it is in contact.

This is the fundamental relation upon which is based the construction of the "molecular gauge" described in the following section.

DESCRIPTION OF GAUGE.

The construction of the gauge is shown in Fig. 1. It consists of a glass bulb B in which are contained a rotating disc A and, suspended above it, another disc C. The disc A is made of thin aluminum and is attached to a steel or tungsten shaft mounted on jewel bearings and carrying a magnetic needle NS. Where the gauge is to be used for measuring the pressure of corrosive gases like chlorine, the shaft and disc may be made of platinum. The disc B is of very thin mica, about

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[1] Ann. Physik, *41*, 289.

[2] B. Baule, Ann. d. Physik, *44*, 145 (1914).

.0025 cm. thick and 3 cm. in diameter. A small mirror, *M*, about 0.5 cm. square is attached to the mica disc by a framework of very thin aluminum. This framework carries a hook with square notch which fits into another hook similarly shaped, so that there is no tendency for one hook to turn on the other. The upper hook is attached to a quartz fiber, about 2×10^{-3} cm. diameter, and 15 cm. long.

"The lower disc can be rotated by means of a rotating magnetic field produced outside the bulb. This field is most conveniently obtained by a Gramme ring (*GG*) supplied with current at six points from a commutating device run by a motor (see Fig. 2). In this way the speed of the motor determines absolutely the speed of the disc, since the two revolve in synchronism. The speed of the disc may thus be varied at will from a few revolutions per minute up to 10,000 or more."

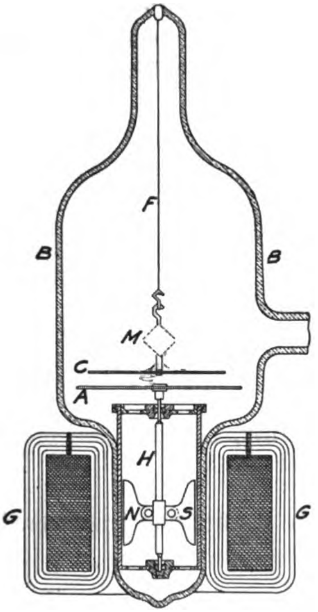

Fig. 1.

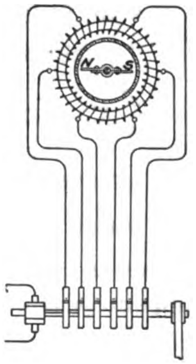

Fig. 2.

Rotating Commutator and Connections to Gramme Ring *G–G* of Fig. 1.

In constructing the gauge, the lower part of the bulb is made to fit an aluminum spring holder which supports the spun aluminum cylinder. The latter contains the upper and lower jewel bearings on which the shaft (*H*) rotates. The bulb is then cut across the widest portion (at *BB*) and the two discs are introduced, care being taken to see that the framework which carries the mirror is not bent during the subsequent re-sealing of the two parts. The quartz fiber is threaded through the hook and a little glass bead attached on the lower end, while the upper end is fastened to a platinum wire by means of sealing-in glass. The last operation consists in "fishing" for the mica disc by means of the hook on the quartz fiber, and after the distance between the two discs has been adjusted, so that the upper disc hangs centrally over the lower disc in a perfectly horizontal plane at a distance of less than 1 cm., the glass at the top of the bulb is closed up around the platinum wire.

One of the great advantages of the gauges as constructed in the above manner is *the complete absence of any parts that cannot be heated up to a temperature of about 300° C. No cement, shellac or other source of vapor should be used in attaching the mirror or the quartz fiber.*

CALIBRATION OF GAGE.

Let r = radius of rotating disc,

ω = angular velocity of rotating disc,

α = angle of torque of upper disc,

D = "Direktions-kraft" on upper disc

$= \frac{\pi^2}{t^2} K,$

where K = moment of inertia of upper disc,

t = period of oscillation.

From equation (15) it follows that the momentum transferred per unit time to upper disc is

$$B_0 = \int_0^r \omega r^2 \cdot 2\pi r dr \cdot kp \sqrt{\frac{M}{RT}}$$

$$= \frac{k\pi r^4 \omega p}{2} \cdot \sqrt{\frac{M}{RT}} \qquad (16)^1$$

$$= \alpha D = \frac{\alpha \pi^2}{t^2} \cdot K.$$

Consequently

$$\alpha = \left(\frac{kt^2 r^4}{2\pi_k}\right) pw \sqrt{\frac{M}{RT}}. \qquad (17)$$

Hence the torque on the upper disc is proportional to the product of the speed of rotation of the aluminum disc and the function $p\sqrt{M/RT}$.

Upon this equation depends the use of the instrument as a sensitive vacuum gauge.

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[1] This equation is only rigorously true if the diameter of the rotating disc is very large compared with that of the upper disc, so that errors due to "edge effect" are avoided.

By properly designing the dimensions of the discs it is evident that equation (17) could be used for *very accurate determinations of the value of k*. In this manner the conclusions of Knudsen, Smoluckowski and Baule on the correction for slip could readily be tested. As the present investigation was carried out mainly with the view of determining the utility of the instrument as a gauge, no such accuracy was attempted so that definite conclusions could not be drawn regarding the value of k. In each case the gauge was calibrated at pressures of about .001 to .01 mm. of mercury against a McLeod gauge. The following data give, however, some idea of the degree of sensitiveness to be expected (and actually obtained) from a gauge constructed on the above principles.

For this particular gauge, the weight of the mica disc was 0.1 gm., $r = 2$ cm., $t = 12$ seconds.

Consequently

$$K = \frac{1}{2} W^2 = \frac{1}{2} \times 0.1 \times 4 = 0.2.$$

Assuming a speed of 1,000 r.p.m.,

$$\omega = \frac{2\pi}{60} \times 1{,}000.$$

In the case of air at a pressure of *1 bar*[1] and 300° Abs., it is found by making the proper substitutions in equation (17) and assuming $k = 1/\sqrt{2\pi}$ that

$$\alpha_{\text{calc.}} = 150^\circ \text{ per bar}.$$

By illuminating the mirror and using a similar arrangement to that used for galvanometers, it is possible to detect a deflection of 1 mm. at a distance of 50 cm. or

$$\frac{1}{500} \times \frac{180}{\pi} \times \frac{1}{150} \text{ bar} = 0.8 \times 10^{-3} \text{ bar}.$$

Increasing the speed to 10,000 r.p.m. increases the sensitiveness tenfold and under these conditions it ought, therefore, to be possible to measure a pressure of about 10^{-4} bar.

Correction Factors.

In using the instrument there are, however, several points regarding which special care ought to be taken.

1. *Correction Due to Eddy Currents in Metal Parts of Mica Disc.*—

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[1] In accordance with most recent practice, we have adopted in this paper as unit of pressure 1 dyne per cm.^{2}. This is known as a *bar*. The relation between this unit and the conventional unit ($1\mu = 10^{-3}$ mm.) is very simple. For all purposes the relation $1\mu = 4/3$ bar is accurate enough. The exact relation is that 1 micron of mercury at 45° latitude and sea-level is equal to 1.01327/.76 = 1.33325 bar.

Owing to the rotation of the magnetic field produced by the Gramme ring, eddy currents are set up in the metal framework used to hold the mirror on the mica disc. Denoting the current through the commutator and Gramme ring by i, the torque actually produced on the upper disc may be expressed as additively composed of two terms, one due to the gas molecules from the rotating disc, and the other due to eddy currents in the metal parts of the upper disc. Consequently, equation (17) assumes the form

$$\alpha = \left(\frac{kt^2r^4}{2\pi K} p\omega \sqrt{\frac{M}{RT}}\right) + k_1 i^2 \omega, \tag{18}$$

where k_1 is a constant for the gauge.

The magnitude of the correction term may be diminished by using metal parts whose electrical resistance is very high and by placing the Gramme ring at a greater distance below the upper disc.

On the other hand, there is really no need for any metal parts whatever in connection with the upper disc. The mirror could be supported in a mica or glass holder, and where extreme accuracy is desired such a construction could no doubt be worked out in detail. For ordinary purposes where it is desired to measure pressures that are not less than 0.001 bar, a framework of thin aluminum wires for holding the mirror introduces no measurable errors.

2. *Synchronism.*—From the construction of the apparatus, it is evident that the aluminum disc rotates five times as fast as the magnetic field. In order to maintain the disc and commutator in synchronism, a rotating sector with five slots in it may be attached to the commutator so as to enable the operator to view a mark on the aluminum disc which should obviously appear to remain stationary if the two are in synchronism. An equally good check is to take readings of the deflection at different speeds. If the speed of the commutator is increased very slowly, there is no difficulty in maintaining the disc and commutator in synchronism.

4. *Relative Position of Discs.*—At a pressure of 1 bar and ordinary temperatures, the mean free path for air is about 10 cm. Consequently, in order that equation (17) should be valid at this pressure, the discs ought to be placed at a distance of less than 1 cm. apart. Care should also be taken to see that the upper disc is located centrally over the lower one. Regarding which disc should be the larger, the following considerations are of interest. In the operation of the gauge there is always a tendency for the upper disc to start swinging or at least get away from its symmetrical position with respect to the lower disc. If the latter is large compared to the mica disc, there obviously results a much greater torque on one side of the disc than on the other and the tendency to

swing is increased until finally the disc hits the walls of the bulb. As the damping at low pressures is very feeble, it is very difficult to stop this oscillation when once started, except by imparting to the bulb itself an opposing motion by hand. After a little experience it is easy in this manner to stop any tendency for the disc to vibrate.

Where it is intended to use the instrument as an absolute gauge or for the determination of k, it is obviously necessary to have the rotating disc much larger. On the other hand, for most purposes, that is where the instrument can be calibrated against say a McLeod gauge at pressures above 1 bar, and used to extrapolate the indications of the latter for very low pressures, it is more advantageous to have the upper disc larger since, in this manner, the tendency to swing is diminished considerably. It must be remembered, however, that as the area of the upper disc is increased beyond that of the lower disc the sensitiveness is decreased.

EXPERIMENTAL.

1. *Preliminary Experiments.*—The gauge used in these experiments contained a much heavier mica disc (weight about 0.5 gm.) and a phosphor-bronze suspension similar to those used in galvanometers. The deflection was determined directly by noting the position of a mark on the mica disc with respect to a circular scale outside the bulb. The molecular gauge was connected in series with a liquid air trap to a Gaede mercury pump and ordinary McLeod gauge.

The following data show that the deflections observed are proportional to the rate of rotation of the aluminum disc. Under p is given the pressure in bars; under r, the rate of rotation in r.p.m., and under A the deflection in degrees. The fourth column gives $D = (A/r) \times 1{,}000$, while the last cloumn gives $D_0 = (A/r) \times 1{,}000/p$, that is, the *deflection per bar at 1,000 r.p.m.*

TABLE I.

p	r	A	D	D_0
0.97	850	18	21	21.3
	1,200	28	23	23
	2,000	44	22	22.5
5.74	1,050	80	76	13.5
	1,750	120	70	12

The reason for the larger value of D at low pressures is probably due to the presence of water-vapor and other condensible gases in the gauge, as the bulb had not been previously baked out.

After allowing dry air to enter the system until the pressure was over

5 mm. of mercury, readings were taken of both the McLeod and molecular gauges, as the pressure was decreased by pumping.

The results of the observations are recorded in Table II.

TABLE II.

p	D	D_0
1,707	990	0.6
960	870	0.9
540	840	1.6
304	820	2.7
171	745	4.0
96	655	6.8
55	490	9
31	360	11.6
24.5	280	11.4
14.0	180	12.8
8	106	13.5
4.7	67	14.3
3.5	46	14.3

It will be observed that up to about 20 bar the deflection was proportional to the pressure. At this pressure the mean free path in air is about 0.5 cm., and this was about the distance between the two discs.

2. *Vapor Pressures of Mercury and Ice.*—For the observations recorded in this section, the sensitiveness of the molecular gauge used was such that $D_0 = 9°$ corresponding to 180 mm. on scale.

The gauge was baked out for one hour at 330° C. and observations then taken on both the McLeod gauge and the molecular gauge under different conditions.

TABLE III.

Press. in McLeod.	D	Press. in Mol. Gage (Calc.).	Remarks.
0.49 bar	23°.7	2.6 bars	Liquid air on trap. Pump not exhausting.
0.8	105.	11.2	Removed liquid air.
0.27	36.4 mm.	0.27	Liquid air on trap and pump exhausting.
1.33	84°	9.3	Removed liquid air.
0.27	36.4	0.27	Liquid air on trap.
0.033	4.5	0.033	Liquid air on trap and pump exhausting.
Removed liquid air.		Stopped exhausting.	
	170 mm.	1.26	At end of 1 minute.
	100°	11.3	At end of 8 minutes.
Put on liquid air again			
	4.5 mm.	0.033	At end of 5 minutes.

It will be noted that the molecular gauge followed changes in pressure which were altogether lost as far as the McLeod was concerned. The pressure of about 10 bar observed on removing the liquid air is evidently due to mercury vapor and non-condensible gases. Allowing about 1 bar for the pressure of the latter (indicated on McLeod) it follows that the pressure due to mercury vapor alone was about 9 bar at room temperature (298° Abs.).

According to Smith and Menzies[1] the vapor tension of mercury between 20° and 30° C. is as follows. (The pressure in bar was obtained by multiplying the pressure in mm. by $4/3 \times 1{,}000 \times \sqrt{200/28.8}$.)

Temperature.	Press. in Mm.	Press. in Bar.
20°	.0013	4.57
24	.00183	6.58
28	.00254	8.92
30	.00299	10.5

The determination of the vapor pressure of mercury as given above is in fair accord with the data for 28°–30° C.

A determination was also made of the vapor tension of ice at − 78° C. A bath of acetone with solid carbon dioxide was put around the liquid air trap and the pressure in the gauge measured while the pump was exhausting. The average of three determinations was 0.9 bar. Allowing for the difference in the temperature of gauge and liquid air trap, the pressure in the latter must have been $0.9\sqrt{195/298} = 0.78$ bar.

Extrapolating from the data given by Scheel and Heuse[2] for the vapor tension of ice at temperatures down to − 68° C., and allowing for the difference in molecular weight of air and water vapor, the pressure at − 78° C. is calculated to be about 0.2 bar. The pressure due to non-condensible gases was not over .05 bar in the above measurement.

3. *Calibration of the Gauge with Hydrogen.*—The theoretical conclusion that the indications of the gauge at constant pressure ought to vary with the square root of the molecular weight was tested by introducing hydrogen into the gauge instead of air.

The gauge used gave a deflection, with air, of 135 mm. per bar at 1,000 r.p.m. The sensitiveness with hydrogen should therefore have been $135 \times \sqrt{2/28.8} = 35$ mm. per bar at 1,000 r.p.m. The actual experiments gave values ranging from 37 to 42 mm.; the discrepancy being probably due to the presence of small quantities of air in the hydrogen used.

4. *Pressure in Tungsten Lamp.*—An ordinary 60-watt type Mazda lamp bulb was connected to a molecular gauge and after exhausting

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[1] Jour. Am. Chem. Soc., *32*, 1447 (1910).

[2] Ann. Phys., *29*, 723 (1909).

them for one and a half hours at 250° C. they were sealed off and pressure observations taken at intervals during the life of the lamp.

The gauge used had a sensitiveness of 1,100 mm. per bar at 1,000 r.p.m. After sealing off and before lighting the filament, the pressure indicated was about 0.8 bar, but as soon as the filament was lighted the pressure decreased and inside of less than an hour it went down to below 10^{-3} bar. The lowest pressure was certainly well below 5×10^{-4} bar, and this determination may be regarded as an upper limit of the probable pressure in a tungsten lamp. It must be noted that the lamp used in these measurements was not given nearly as good a heat treatment as in the usual lamp exhaust.

The fact that the vacuum in a tungsten lamp improves when the filament is lighted has been known for some time, and the causes of this "clean-up" effect have been discussed in a number of papers published during the past three years by I. Langmuir.[1]

As the volume of the gauge was only slightly greater than that of the lamp bulb, we can conclude that the pressure obtained in a well-exhausted tungsten lamp, when the filament is lighted, is certainly well below 10^{-3} bar.

5. *Experiments with the Gaede Molecular Pump.*—A Gaede molecular pump[2] was run in series with an oil pump which in turn was connected to the "rough vacuum" line. A McLeod gauge was inserted between the oil pump and molecular pump in order to read the pressure on the rough side of the latter.

A liquid air trap was arranged between the gauge and the pump so that the diffusion of vapor of stopcock grease or of water could be prevented.

The following table shows the results obtained under different conditions:

No.	Press. on Rough Side of Molecular Pump.	Press. on Fine Side, Read by Molecular Gauge.	Conditions of Experiment.
1	13.3 bar	0.20 bar	After exhausting for 1 hour. No heating of gage; no liquid air.
2	13.3	0.09	Put on liquid air.
3	13.3	0.033	Heated gage to 300° C. for 1 hour, but did not heat glass tubing between gage and pump.
4	1,333	0.033	Let in dry air on rough side. Press. on fine side remained constant. Ratio = 40,000:1.
5	20,000	0.4	Let in more air on rough side. Ratio = 50,00:1.
6	20	$\ll 0.0007$	Ratio 30,000:1.

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[1] J. Am. Chem. Soc., *35*, 107 (1913), et sub.

[2] W. Gaede, Ann. Physik, *41*, 337 (1913).

It is evident from experiment (3) that heating the gauge alone was not sufficient to reduce the pressure in it owing to the constant diffusion of water-vapor from the tubing between the gauge and liquid air trap. But after this tubing had been also heated to 330° C. (experiment 6) the pressure in the gauge went down below 7×10^{-4} bar.

The sensitiveness of the gauge employed was such that 1 bar gave a deflection of 525 mm. at 1,000 r.p.m. At very low pressures a correction term had to be introduced for the eddy current effect in the framework of the mirror. The equation connecting pressure (p) and deflection (D) may be written in the form

$$D = \frac{525}{1000} p.r. + k i^2 r, \tag{19}$$

where r = revolutions per minute, and k is a constant. See equation (18).

By noting D for different values of r and i, while p is maintained constant, it is possible to determine the value of k, and hence introduce the proper correction into the calculation for p. A special series of experiments showed that in the case of the above gauge, the equation for calculating p was of the form:

$$p = \frac{D}{0.525r} - 29 \times 10^{-5} i^2.$$

The value of i varied from 3 to 5 amperes. It is evident that the presence of this eddy current effect limited the sensitiveness of the gauge, for even at zero pressure, the deflection at 4 amperes and 10,000 r.p.m. would be 24 mm. At 7×10^{-4} bar, the deflection at 10,000 r.p.m. and 4 amperes would be 27.6 mm.

Under the best vacuum conditions, that is, using liquid air, and heating the gauge and all connecting parts to over 330° C. for about one and a half hours or longer, the deflections actually obtained were only slightly greater (1 or 2 mm. more) than the correction due to the eddy current effect. Allowing for experimental errors and for the difficulty in reading to an accuracy of 2 mm. when the disc was rotated at very high speeds, it is probably correct to conclude that the vacuum obtained was less than 7×10^{-4} bar. Assuming the ratio of 50,000 : 1 as holding down to the very highest vacuum conditions, the vacuum attained in the gauge with a pressure of 20 bar on the rough side should have been 4×10^{-4}. The experimental observations are in satisfactory agreement with this calculation.

It is worth noting in this connection that in his paper describing the construction of the molecular pump, Gaede states that (at 8,200 r.p.m.)

with a rough pump pressure of 1 mm. he obtained a pressure of .02 μ on the fine pump side corresponding to a ratio of 50,000 : 1. Both pressures were read by means of McLeod gauges.

OTHER VACUUM GAUGES.[1]

In this connection it might not be amiss to mention briefly some of the other vacuum gauges that have been suggested for the measurement of pressures below 1 bar.

1. The radiometer has been used by a large number of investigators. Dewar has stated the case for this instrument as follows:[2] "The radiometer may be used as an efficient instrument of research for the detection of small gas pressures. For quantitative measurements the torsion balance or bifilar suspension must be employed."

Some years ago Mr. W. E. Ruder, of this laboratory, developed a method of using the radiometer for the measurement of the gas pressure in incandescent lamps. "It was found that when exhausted to the degree required in an incandescent lamp the radiometer could not be made to revolve, even in the brightest sunlight. In order to get a measure of the vacuum, the radiometer vanes were revolved rapidly by shaking the lamp and the time required to come to a complete stop was therefore a measure of the resistance offered to the vanes by the gas, together with the frictional resistance of the bearing. The latter quantity was found to be so small in most cases that a direct comparison of the rates of decay of speed of the vanes gave a satisfactory measure of the degree of evacuation. In this manner a complete set of curves was obtained which showed the change in vacuum in an incandescent bulb during its whole life and under a variety of conditions of exhaust.

"The chief objections to this method of measuring vacua were the difficulty in calibrating the radiometer and the difference in frictional resistance offered by differnet radiometers. For *comparative* results, however, the method was entirely satisfactory."[3]

2. Scheele and Heuse[4] devised a manometer which has been used successfully for the accurate determination of the vapor pressures of mercury and ice at very low temperatures. This gage consists of two chambers separated by a copper membrane. One of the chambers is

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[1] A good description of some of the gages mentioned in this summary is given in K. Jellinek's recently published "Lehrbuch der Physikalischen Chemie," I, 1.

Shortly after this paper was sent to the printer, a description of a modified Knudsen manometer was published by J. W. Woodrow, Phys. Rev. 4, 491 (1914). The sensitiveness of this gage is stated to be about 4×10^{-5} bar.

[2] Proc. Roy. Soc., *A*, *79*, 529 (1907).

[3] This account was kindly prepared by Mr. Ruder at the request of the writer.

[4] Ber. d. deutsch. phys. Ges., 1909, 1–13.

maintained at constant pressure while the other is connected to the system under investigation. The membrane presses on a glass plate and the variation in the thickness of the film is measured by noting the number of interference bands.

3. The McLeod gauge can be constructed so that it is sensitive to 0.01 bar. Its field of application is however necessarily limited.

4. Pirani[1] has suggested a resistance manometer which depends upon the fact that at low pressures the heat conductivity of gases is a function of the pressure. In consequence of this change in the heat conductivity, the apparent resistance of the wire changes with pressure of the gas surrounding it. The method has been improved by C. F. Hale[2] and the manometer has been found to give reliable results down to 0.00001 mm. of mercury, that is to about 0.01 bar.

5. Very recently W. Rohn has described a vacuum meter based on almost the same principles.[3] In this case the effect on the thermo-electromotive force of varying gas pressure is used as a method of determining very low gas pressures. The instrument is most sensitive between about 100 and 1 bar (0.075 mm. and 0.00075 mm. of mercury) the electromotive force varies approximately linearly with the logarithm of the pressure. At lower pressures, the sensitiveness diminishes quite rapidly.

6. Haber and Kerschbaum have used vibrating quartz fibers to measure the pressure of mercury and iodine.[4] This method was originally suggested by I. Langmuir[5] for measuring the residual gas pressure in sealed-off tungsten lamps and has been in use in this laboratory for about three or four years. As the pressure decreases the duration of the oscillations increases. Haber and Kerschbaum have deduced a relation between the pressure p and the interval t in which the vibration decreases to half its original amplitude, as follows:

$$\Sigma(p\sqrt{M}) + a = \frac{b}{t},$$

where a and b are constants and Σ denotes that the sum of the products of partial pressure and square root of the molecular weight is to be taken for each gas present. The lowest pressures actually measured by the above authors were about 0.015 bar, but the method has been used in this laboratory by Dr. Fonda to measure pressures considerably smaller than this.

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[1] Ber. d. deutsch. physikal. Ges., 1906, 686.

[2] Trans. Am. Electrochem. Soc., *20*, 243 (1911).

[3] Z. f. Elektrochem., *20*, 539 (1914).

[4] Z. f. Elektrochem., *20*, 296, 1914.

[5] J. Am. Chem. Soc., *35*, 107, 1913.

7. W. Sutherland[1] and, subsequently, J. L. Hogg[2] derived simple relations between the pressure and the logarithmic decrement of a vibrating mica disc. The gauge based on this principle requires calibration at two known pressures, and is not very sensitive below about 0.01 bar.

8. M. Knudsen as the result of an elaborate study of the laws of "Molekularströmung" devised an absolute form of manometer[3] which depends upon the fact that at very high vacua there exists a very simple relation between the pressure and the torque imparted to a movable surface by the molecules flowing to it from a hotter surface. This relation has the form

$$K = \frac{p}{2}\left(\sqrt{\frac{T_1}{T_2}} - 1\right),$$

where K denotes the force of repulsion between two surfaces maintained at temperatures T_1 and T_2 respectively in a gas at pressure p. From the dimensions of the movable disc and the period of oscillation of the suspension, the value of K may be calculated and the gauge may therefore be used without any previous calibration. Knudsen uses this guage to indicate pressures as low as 2×10^{-3} bar.

9. Still more recently[4] Knudsen has devised a simplified form of vacuum guage, based on the same principles as the above, which he states to be sensitive to 2×10^{-4} bar.

Concluding Remarks.

The vacuum gauge described above might obviously be used to determine the magnitude of the "accommodation coefficient" for different gases, and thus test out the deductions advanced by different investigators.

Another line of investigation for which the gauge would be useful is the determination of the vapor tension of oils, waxes, etc., such as are used in connection with vacuum work. Owing to pressure of other work the writer has been prevented till now from carrying on such an investigation; but the results would be of great practical utility, as these materials are being constantly used by experimenters in connection with so-called "high vacuum" experiments.

In conclusion the author desires to express his appreciation of the

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[1] Phil. Mag., *43*, 83 (1897).

[2] Proc. Am. Acad., *42*, 6 (1906); Phil. Mag., *19* (1906); Proc. Am. Acad., *45*, No. 1, Aug., 1909.

[3] Am. Physik *32*, 809 (1910).

[4] Am. Physik *44*, 525 (1914).

kindly interest shown by Dr. I. Langmuir during the progress of the investigation and for helpful suggestions.

SUMMARY.

A theoretical consideration of the behavior of gases at very low pressures shows that a rotating disc exerts a torque on a disc suspended symmetrically above it, that is proportional to the quantity $\Sigma(p\sqrt{M/RT})$. Here p denotes the partial pressure and M the molecular weight of each constituent present in the gas and R and T have their usual signification.

The paper contains the description of a vacuum gauge based upon this principle, and also the results of a number of measurements carried out with its aid.

It was found that in order to obtain the best possible results with a Gaede molecular pump, it is necessary not only to heat the vessel to be exhausted and connecting tubing to a temperature at which most of the moisture adsorbed in the walls is driven out, but also to insert a liquid air trap to prevent the diffusion backwards of condensible vapors.

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FLICKER PHOTOMETER MEASUREMENTS BY A LARGE GROUP OF OBSERVERS ON A MONOCHROMATIC GREEN SOLUTION.

BY HERBERT E. IVES AND E. F. KINGSBURY.

A DETERMINATION of the mechanical equivalent of light, now in progress, demanded the photometric evaluation of the monochromatic green radiation of the mercury arc, wave-length .5461 μ. Since in measuring the luminous intensity of a colored light in terms of the present yellowish white standards it is always necessary, no matter what method of visual photometry is employed, to use a large number of observers, some means was necessary to determine that value by a separate experiment. It is well known that the current-intensity relation in the mercury arc is not nearly reliable enough to permit of holding the radiation constant by maintaining the current at a fixed value. It was therefore necessary that our measurements be made on some auxiliary standard which would possess maintainable and reproducible characteristics. For this standard we decided upon an absorbing solution, which should be used over the standard "4-watt" carbon lamp, to be of such constitution that the transmitted light would be a visual match with the green mercury light. Such a solution was developed and used. The details of its use and the results of its measurement have points of interest apart from the question of the mechanical equivalent of light and are, therefore, presented here separately.

THE ABSORBING SOLUTION.

The solution, which transmits light exactly matching the green line .5461 μ when used over a standard carbon lamp, is a mixture of potassium dichromate and cupric chloride, together with a sufficient amount of nitric acid to hold the two in solution. The composition for 25 millimeters thickness is:

Potassium dichromate	2.5 grams.
Cupric chloride	265.0 grams.
Nitric acid (sp. gr. 1.05)	26.5 cu. cms.
Water to one liter.	

The cupric chloride before weighing is dried by being raised to a temperature of 50° centigrade. When mixed the solution is filtered through a triple paper filter.

Careful photometric tests have shown that with these precautions the solution is absolutely reproducible and, certainly over periods of several weeks and probably much longer, shows no detectable fading or other change.

In the use of the solution it is necessary to know its change of transmission with change of temperature. This has been determined by comparison on the photometer of the light through a solution at the standard temperature of 20 degrees centigrade with that through another at various higher and lower temperatures. The values are shown in Fig. 1.

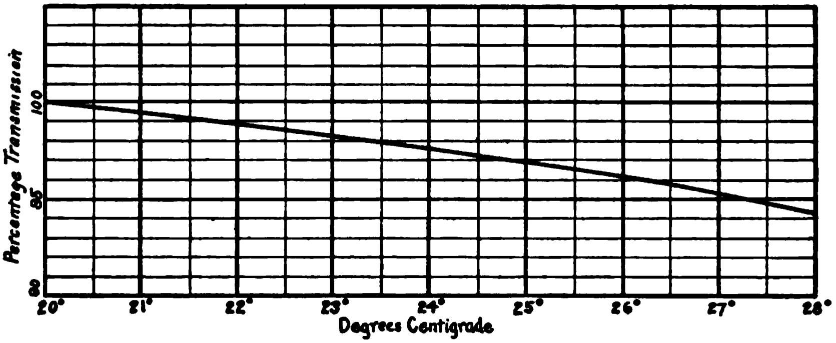

Fig. 1.

Temperature Coefficient of Transmission of Green Solution.

The Absorption Cells.

Great emphasis must be placed on the importance of using a reliable type of absorption cell. In a recent investigation we have found differences of as much as five per cent. in the transmission of supposedly similar clear glass tanks. As a result of our study we have come to the use of a special type of tank, shown in Fig. 2. The solid glass frame is exactly 25 millimeters thick, in this case, and can be obtained without difficulty from a good glass worker. The two removable faces must be selected with the greatest care, for upon them depends the value of the

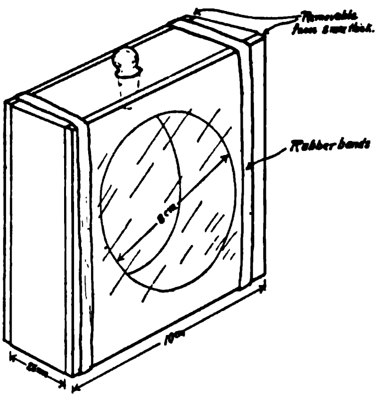

Fig. 2.

Type of Absoiption Cell Used.

cells' transmission. We are using plates two millimeters thick, of special clear white glass which shows no color when viewed edgewise. In addition, we have tested these glasses through the spectrum by means of approximately monochromatic color screens on an ordinary Lummer-Brodhun contrast photometer, finding no selective absorption.

The cleaning and handling of these faces is also of importance. Whenever removed they are washed with hot water and soap, rinsed thoroughly with hot water and wiped carefully with a clean soft towel free from grit. After cleaning they are laid against the glass frame, held in place with rubber bands, and a seal of paraffine run around the edges with a hot metal spoon to prevent the cell from leaking. The solution, or the clear water as the case may be, is introduced through the stoppered opening at the top.

In order that the necessary cleaning and the inevitable process of surface decay shall not introduce progressive and unnoticed differences between the cells used they should be periodically compared for their total transmission when filled with clear water, and if it becomes necessary, new faces should be obtained.

THE METHOD AND DETAILS OF THE MEASUREMENT.

The transmission of this solution was measured by means of the special flicker photometer recently described in the PHYSICAL REVIEW.[1]

The conditions of measurement were those determined upon as a result of the extended study of colored light photometry by one of the present writers, involving the maintenance of one field brightness throughout, the use of a small field and other details for which reference may be made to the work quoted.[2]

The experimental procedure was as follows: The flicker photometer was mounted at one end of a three-meter photometer bar. The carbon lamp, a 100-candle-power point source of the stereopticon type, carefully matched in color with a standard supplied by the Bureau of Standards, was upon a movable carriage. The absorption cells, one containing clear water, the other the green solution, were held in supports before the photometer. The first measurement was upon the transmission of the clear water. The lamp was set at such a distance from the photometer screen that the brightness of the photometer field was that of a white surface illuminated by 25 meter-candles. After five settings were made with the clear solution it was replaced by the green one, and the lamp moved to a nearer position so that the new measurement was carried

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[1] PHYSICAL REVIEW, October, 1914.

[2] Photometry of Lights of Different Colors, Phil. Mag., July–December, 1912.

out at approximately the same field brightness. Five settings were made on this and then the process was repeated so that each observer made ten settings. Between groups of settings the green solution was immersed in a basin of water held at 20 degrees centigrade, on removal from which it was wiped dry with a clean soft towel. From the relative distances of the lamp, correcting for the thickness of glass and water, the transmission of the solution, compared with clear water, is obtainable.

This description refers to a single observer. In order that the result may apply to the average eye, it is necessary to secure values from a large number, just how large a number being one of the points to be determined by the investigation. The measurements here recorded were on some sixty-one observers, members of our laboratory force employees of other departments of the company, and some visitors. Many of the subjects were new to photometric reading, the majority had never read a flicker photometer. The determinations extended over a period of about two months.

No other tests of color vision were made so that it is possible we have among the number some whose vision might be classed as abnormal. We are reasonably sure that none is included who would fall in the classification of "color blind," because measurements made on one known color-blind person gave a result 60 per cent. larger than the mean, falling in a class entirely apart. The observers probably constitute an "average" group of men and, as will be seen, the number is apparently large enough so that the addition or subtraction of any chance observer or any group chosen at random would leave the mean value substantially the same.

Results.

In Fig. 3 are plotted the results obtained by the observers in the order taken, together with the mean of all values up to each point. The final mean value for the transmission of this solution at 20 degrees centigrade, compared with clear water, is .0437. Individuals vary from this as much as sixteen per cent. above, and twenty-nine per cent. below (leaving out of account the color-blind observer above mentioned).

Discussion.

The question of the precision and reproducibility of measurements of this kind has been discussed quite fully in the previous papers. The present measurements merely confirm the previous findings. Repeat measurements were made on some of the observers, with results checking to about one per cent. About a third of the observers had previously taken measurements on a similar but ultimately unsatisfactory solution.

Their relative positions with respect to the mean were the same on that series and on this with only a few slight changes in order, showing that no considerable changes in an observer's criterion are to be looked for.

We have searched in vain for any connection between the position of an observer in this series and any of his physical characteristics, such as age.

A point of extreme importance in colored-light photometry is here demonstrated in very convincing form. This is that precision in reading and agreement between different observers of a small group are no evidence whatever of accuracy. The emphasis placed upon this is prompted by the widely-found belief that if one observer reads with a small mean variation and consistently from time to time it is evidence that his readings are "right"; and the similar idea that if several observers who happen to be associated together read alike, their result must be "right." This conclusion is valid only where there is no color difference. Where there is a color difference, only some such investigation as that here reported can be established what is to be taken as correct. The correctness of an individual observer's setting has nothing whatever to do with his skill or training—it is dependent upon the color sensibility of his retina. The agreement of several observers is a matter of chance, except where, using the equality of brightness or direct comparison

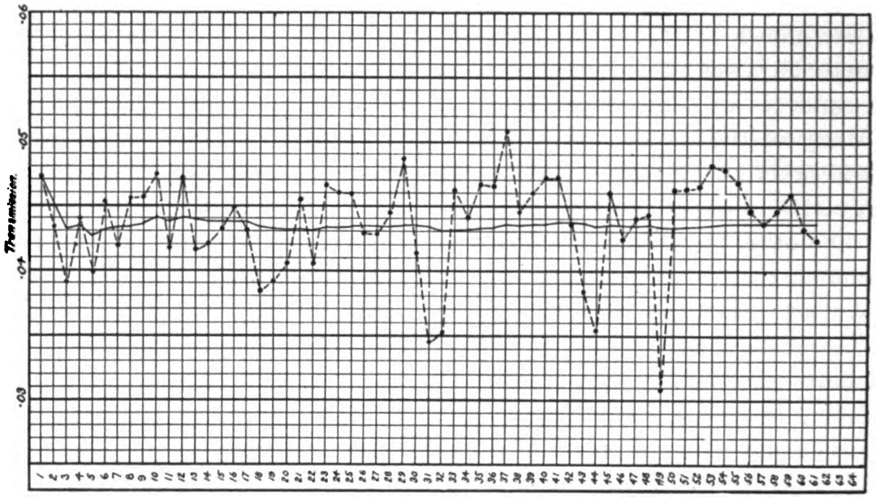

Fig. 3.

Individual Readings on Transmission of Green Solution.
Points,—observations.
Numbers,—observers.
Solid line,—mean of all observations up to and including point.

method, observers have consciously or unconsciously altered their criteria toward a common mean. The justice of this criticism is strikingly illustrated by the fact that observers 51, 52, 53, 54 and 55 constitute the entire group of photometrists from a laboratory in which measurements involving a considerable color difference were part of the regular routine. They agree with each other to within about three per cent. but their mean on this particular color difference is eight per cent. above the average for all.

These considerations indicate the importance of a definite scheme of selecting observers from a group of at least twenty-five or thirty where lights of different color are to be evaluated. They also emphasize the desirability of methods of colored-light photometry by which individual observers may secure the results of the average eye as established by measurements on a large group. We expect to report shortly on means for achieving this end.

Physical Laboratory, The United Gas Improvement Company,
Philadelphia, November, 1914.

ISOLATED CRYSTALS OF SELENIUM OF THE SECOND AND FIFTH SYSTEMS, AND THE PHYSICAL CONDITIONS DETERMINING THEIR PRODUCTION.

By F. C. Brown.

RECENTLY[1] I described new crystal forms of metallic selenium, in connection with their optical and photo-electrical properties. One form was definitely classified as belonging to the rhombohedral hexagonal system, but because of the smallness and incompleteness of the lamellar crystals they could not be classified. Since then we have succeeded in obtaining lamellar crystals well developed on all surfaces, so that the angles between all faces could be determined with a certain accuracy, by the use of a circle goniometer.

The reproduction in Fig. 1 is that of lamellar crystals belonging to the fifth or monoclinic system. A diagram of one of the crystals is given in Fig. 2, together with the plane of symmetry and the axes. The surfaces m, n and O are at right angles. The ratios of the axes of one crystal were about $a : \bar{b} : c = 1.0 : 0.18 : 6.0$, $\beta = 60°$. The longest crystal was about 10 mm.

Crystals of the hexagonal system were photographed and reproduced in the previous article referred to. In the acicular crystals the angles between the faces were all 60°. Other crystal forms and growths were reproduced but thus far it has not been possible to definitely classify them.

Crystals of both systems were produced by sublimating amorphous selenium after it had been melted. In general the higher the temperature at which the crystals were formed from the vapor, the more certainly would the hexagonal needles form. At temperatures between 190° and 220° large quantities of the hexagonal needles were obtained, and at the highest temperature various undetermined forms and combinations of forms appeared. It required one or two weeks for the crystals to form in the larger sizes.

By keeping the oven temperature at 170° ± 1° for a period of three months the monoclinic crystals shown in Fig. 1 were made. The selenium vapor was driven from the amorphous form at a somewhat higher temperature and condensed on the crystal at the above temperature. These

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[1] PHYS. REV., N. S., Vol. 4, p. 85, 1914.

Physical Review, Vol. V., Second Series.
March, 1915.

Plate I.
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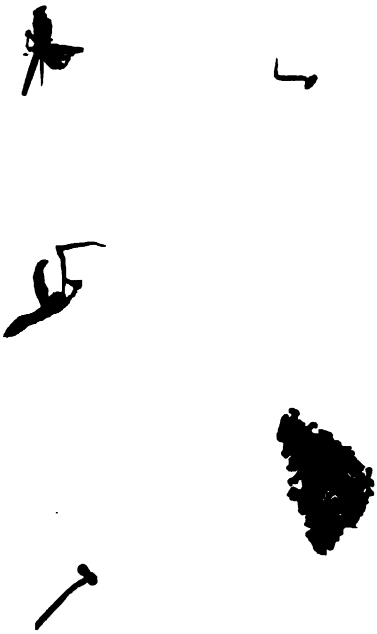

Fig. 1.

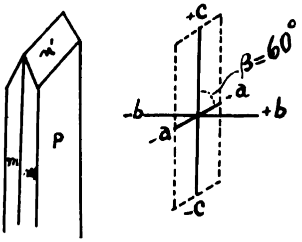

Fig. 2.

F. C. BROWN.

crystals were formed in a vacuum, except for the selenium vapor present. It was observed that these lamellar crystals would also form at temperatures as high as 190° in an atmosphere of air at normal pressure. Also it seemed necessary to increase the temperature necessary for the formation of the hexagonal form when the vapor was deposited in air at normal pressure. These observations lead to the supposition that the vapor density as well as the temperature is a determining factor in the control of the crystal forms.

As far as has been tested the electrical, the light-electric, and the electro-mechanical properties of the selenium crystals of the two systems do not show any distinct differences. The value of the conductivity, and the sensibility to light in different parts of the spectrum are of the same order of magnitude. The above facts indicate that the above properties are seated in the molecular structure, and that the minor variations are controlled by the crystal structure.

It has been observed that the light on going through the wedge-shaped end of a lamellar crystal is deviated about 30°. Since we know the angle of the wedge, we have a direct method of measuring the index of refraction of a conducting substance. This will be carried out at the earliest opportunity.[1]

University of Iowa.

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[1] Since writing this article I have obtained the red crystalline variety of selenium by sublimation. These crystals are doubly refracting and are no doubt the same as those obtained by various chemical means. The precise physical conditions *i. e.*, vapor pressure and temperature. governing the formation of the red crystals by sublimation are yet to be determined.

THE INTENSITIES OF X-RAY SPECTRA.

By David L. Webster.

According to Bragg[1] if X-rays of a given frequency are reflected from a crystal at the angle θ, the intensity of the reflection may be expressed within the limits of experimental error by the equation

$$I_\theta = \frac{A(1 + \cos^2 2\theta)}{\sin^2 \theta} e^{-B \sin^2 \theta}. \tag{1}$$

The constant A depends on the kinds and numbers of atoms in the crystal and the intensity and frequency of the incident rays, while B depends on the thermal properties of the crystal. The exponential factor has been found by Debije[2] to result from displacements of the atoms from their normal positions by heat vibrations. The factor $(1 + \cos^2 2\theta)$ originally deduced by Thomson[3] for any kind of secondary X-radiation, results from the fact that the component of vibration of the electron perpendicular to the plane of the incident and reflected beams will make it radiate equally in all directions in that plane, while the other component, being perpendicular to the incident beam but not to the reflected one, will make the amplitude of the secondary radiation vary as the cosine of the angle between the beams, that is, as $\cos 2\theta$. Adding the squares of the amplitudes, one obtains the factor $(1 + \cos^2 2\theta)$ in the expression for the reflected energy. This factor suggests some interesting experimental possibilities, which will be discussed below.

The factor $\sin^2 \theta$ in the denominator, as Professor Bragg has recently told me, has not yet been accounted for. The object of this paper is therefore to account for it, and to show that it signifies that the train of waves emitted by an atom in the radiator is short compared to the distance the rays travel through the crystal. This, as a matter of fact, does not seem very unreasonable when we consider the origin of the rays, in the impacts of cathode particles against these atoms. The possibility of a further experimental test of this result is discussed below.

Reflection of a Long Train of Waves.—Since Debije[4] has found that

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[1] W. H. Bragg, Phil. Mag., 27, 895, 1914.

[2] Verh. d. Deut. Phys. Ges., 15, Nos. 15 and 16, 1913.

[3] J. J. Thomson, The Conduction of Electricity through Gases.

[4] L. c.

the heat motion of the atoms should not affect the sharpness or position of the reflection, and should change the intensity only by the factor $e^{-B \sin^2 \theta}$ we shall treat the atoms as though they were stationary, and insert this factor at the end. We shall also consider only the vibration components perpendicular to the plane of incidence, and insert the factor $(1 + \cos^2 2\theta)$ in the final expression for the reflected energy. We shall consider first the case of reflection of a train of waves from a single layer of atoms at an arbitrary angle θ, and then take account of the influence of the different layers upon each other, treating the case of a very long train first, and then that of a short one.

In the accompanying figure, S represents the source of rays, S' its image in the plane $P'P''$, containing the atoms, and O the observing point. To find the intensity of the reflected beam, we must take account of the components of electric force from each atom in the plane, paying especial attention to their phases. This may be accomplished best by treating the waves as though they came from the image S' and were reradiated from the various atoms, but not otherwise propagated through the plane.

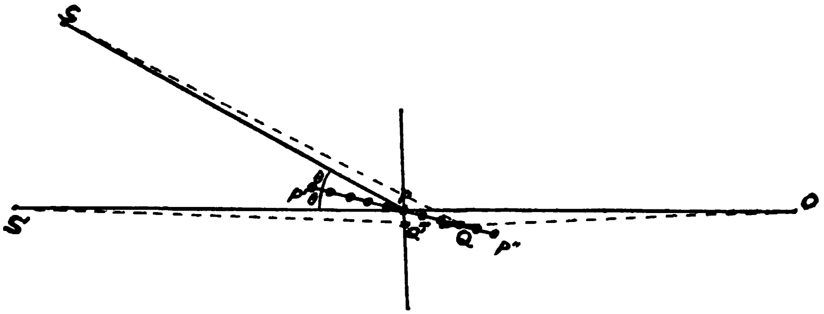

Fig. 1.

For the radiation from the atom Q, whose distance from P is small compared to PO or PS, we may find the phase retardation, relative to that from P, as

$$2\pi \frac{\overline{S'Q} + \overline{QO} - \overline{S'O}}{\lambda},$$

λ being the wave-length of the rays. This evidently is the same, except for small quantities of a higher order, as if Q were replaced by its projection, Q', on the plane through P perpendicular to PO. Projecting all the positions of the atoms in this way, we obtain on the plane PQ' a uniform distribution of points, of a surface density $Na/\sin\theta$, where N is the volume density and a the distance between the planes.

Thus the problem resolves itself into one almost exactly similar to the application of Huygens's principle of light to the case of a spherical wave spreading from the image S'. For it is well known, that for cases where $S'P$ and PO are large compared to the wave-length, an approximate form of this principle applied to the plane PQ' is obtained by supposing the ether to absorb and re-radiate the energy coming to it just as the atoms do here. This, in fact, is the form in which the principle is usually stated in textbooks on optics. In this case, however, the effect of any surface element dS in the plane PQ' is the electric force radiated from the atoms, $NadS/\sin\theta$ in number, whose projections lie in this element. Therefore, since the distance between atoms (about 10^{-8} cm.) is small compared to the radius of the first quarter wave zone (10^{-3} to 10^{-2} cm.), and this in turn is small compared to the distances to S' and O, we may say without further computation that the reflected amplitude at O will be proportional to the surface density, $Na/\sin\theta$, of the projections of the atoms on the plane PQ'. For this result it is not necessary to assume that θ is an angle of reflection for the crystal as a whole.

Thus if the amplitude of the electric force of the incident wave is E_i, that of the reflected one from a single layer will be

$$qE_i\frac{Na}{\sin\theta}, \tag{2}$$

where q is a coefficient expressing the reflecting power per unit surface density of the atoms, and depending on their weight and structure.

If the reflections from successive layers are not retarded by an integral number of wave-lengths, they will of course cancel each other; but if they are thus retarded, they will reenforce. This leads to the well-known equation,

$$n\lambda = 2a\sin\theta, \tag{3}$$

for the value of θ giving the reflection of order n and wave-length λ.

Since the rays are absorbed in entering the crystal to the point P, we have

$$E_i = E_0 e^{-kx}, \tag{4}$$

where x is the distance the incident wave has come through the crystal; and since the reflected wave is absorbed in the same ratio before it emerges, its amplitude at the point O is

$$qE_0\frac{Na}{\sin\theta}e^{-2kx}. \tag{5}$$

In the case of reflection at the proper angle, we must now sum these amplitudes from all the planes. Replacing x by $y/\sin\theta$ so that y is the depth of the plane from the face of the crystal, and replacing a by dy, we may turn the summation into the integral,

$$qE_0 \frac{N}{\sin \theta} \int_0^Y e^{-\frac{2ky}{\sin \theta}} dy = \frac{qE_0 N}{2k} (1 - e^{-\frac{2kY}{\sin \theta}}). \tag{6}$$

Therefore, if kY is large, as it generally is, this is independent of θ, and long trains of waves will not give the $\sin^2 \theta$ in the denominator of expression (1).

If the crystal is composed of small pieces, each acting independently, then we might assume that the rays would go through one piece with no appreciable loss, and would therefore be reflected from it in proportion to $1/\sin^2 \theta$. This may be seen from the fact that the number of reënforcing layers would then be constant, and equal to the whole number in the uniform piece of the crystal.

Here, however, we should have to remember that the rays would still penetrate with a given intensity to a depth proportional to $\sin \theta$, so that the number of pieces of the crystal that reflect would vary in that way. Since they would all reflect independently, we should have to add reflected energies, rather than amplitudes, and the resulting energy would be proportional to $1/(\sin \theta)$ rather than to the $1/(\sin^2 \theta)$ given by experiment. Thus it appears that the long train hypothesis must be abandoned.

This result has been obtained also by Darwin,[1] but the calculation is given here because it is of interest in what follows.

Short Trains of Waves.—Turning now to the opposite hypothesis, that the trains of waves are short compared to the distance they go through the crystal, and until further notice considering the crystal uniform, we may make use again of the expression (2) for the amplitude reflected from a single plane. In this case, however, the calculation of the number of reënforcing planes is more complicated.

For simplicity, let us consider a single train, of M waves, reflecting in the nth order. At the instant when the nth wave of the reflected train from a given layer of atoms arrives at the point O, the wave arriving from the next layer above is the $2n$th, and the one from the layer above that is the $3n$th, and so on. Thus the total number of reënforcing layers is not M, but M/n; and neglecting the change of amplitude of the incident wave by absorption in going the length of the train, the whole reflected amplitude is

$$\frac{M}{n} qE_i \frac{Na}{\sin \theta} e^{-kx},$$

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[1] C. G. Darwin, Phil. Mag., 27, 675, 1914.

where e^{-kz} is the fraction that is not absorbed before leaving the crystal, and E_i itself is E_0e^{-kz}. Thus, for a given value of x while the reflected train is passing O, its amplitude will be proportional to $a/(n \sin \theta)$, or to $1/(\sin^2 \theta)$, so that the energy density in it varies as $1/(\sin^4 \theta)$.

The length of this train, however, will depend, not on that of the incident one, but on the distance it penetrates into the crystal and the relative retardation of the waves from the surface and from the lower layers. Therefore, to find the whole reflected energy, we must evaluate the energy density at a given distance from the front of the reflected train, and integrate over its whole length. Since the mean energy density over a whole wave is $1/8\pi$ times the square of the amplitude of the electric vibration, and the retardation of the part of the train reflected from the depth y (that is, the distance from the front of the reflected train) is $2y \sin \theta$, the whole energy is

$$\frac{1}{8\pi}\left(\frac{M}{n} qE_0 \frac{Na}{\sin \theta}\right)^2 \int_0^\infty e^{-\frac{4ky}{\sin \theta}} \cdot 2 \sin \theta \, dy = \frac{1}{16\pi k}\left(\frac{M}{n} qE_0Na\right)^2.$$

Since $n\lambda = 2\, a \sin \theta$, we may write this as

$$\frac{M^2\lambda^2q^2E_0^2N^2}{64\pi k \sin^2 \theta}, \tag{7}$$

thus showing that the resultant energy from any short train is proportional to $1/(\sin^2 \theta)$ for all faces of the crystal that have uniform distances between the planes. Moreover, since a does not appear in (7), this explains the fact that this proportionality holds whether the distances are the same for different faces or not.

To improve this expression (7), let us note that $\frac{1}{8\pi} E_0^2L$ is the intensity I, of the incident train, and $M\lambda$ is the whole length, L, of the wave train. Introducing these substitutions and the factors $(1 + \cos^2 2\theta)$ and $e^{-B \sin^2 \theta}$ mentioned above, we have as a final expression for the reflected energy

$$\frac{Iq^2LN^2(1 + \cos^2 2\theta)}{8k \sin^2 \theta} e^{-B \sin^2 \theta}. \tag{8}$$

This shows that in Bragg's formula

$$A = \frac{IqL^2N^2}{8k}. \tag{9}$$

Since according to the short train hypothesis, there is no reënforcement of waves from very different depths, the assumption made above, that the crystal is uniform, is not essential if the uniform pieces within it are large compared to the lengths of the trains of waves. Thus (8) is really independent of the uniformity of the crystal.

Since (8), rather than (6), is verified by experiment, we may conclude that the trains of waves are really short compared to the distances they penetrate into the crystal, or, if the crystal is not uniform, they must be short compared to the irregularities in its structure.

A further experimental test of this short train hypothesis should be found in measurements of the reflecting power of a crystal for rays which have already been reflected once. Such waves, being in long trains, should show less difference in the intensities of different orders than in the first reflection, provided that the first crystal is really uniform enough to give a long train of reflected waves. Moreover, under these conditions, the larger value of L in a train that has already been reflected once should make the reflection coefficient greater in the second reflection than in the first. The apparatus to test these points is now being constructed.

The Polarization of Reflected X-Rays.—Another point to be tested is the polarization of the reflected rays that is assumed in deriving the factor $(1 + \cos^2 2\theta)$ in equation (1). This factor, as we have seen, is due to the fact that in the plane of incidence each atom scatters the component of the electric vibration perpendicular to that plane equally well in all directions, while the other component is diminished at the angle 2θ from the original beam, by the ratio $\cos 2\theta$. Thus the intensities of the two components will be in the ratio of 1 to $\cos^2 2\theta$.

If now the beam is reflected twice in a horizontal plane, the ratio of the intensity of the vertical component to that of the horizontal one after the second reflection will be 1 to $\cos^4 2\theta$, and the intensity of the resulting beam will bear the ratio $(1 + \cos^4 2\theta)$ to that of the vertical component, which we may take as the standard. If, on the other hand, the second reflection is in a vertical plane, the vertical component will then be diminished, so that the intensity of each will be the fraction $\cos^2 2\theta$ of the above standard, and the whole intensity will be $2 \cos^2 2\theta$.

If now θ is as large as 20°, as in some of Bragg's experiments, the ratio of the total intensities in these two cases will be 1.171 to 0.826. At larger angles, if the intensity is not too weak, such measurements should show an even greater difference, and at $\theta = 45°$, the vertical reflection would be impossible, as the beam would then be totally plane-polarized.

SOME SECONDARY EFFECTS FROM ROENTGEN RAYS.

By Paul T. Weeks.

In an article in Science (38:347–8) F. R. Gorton describes an anomalous effect obtained with Roentgen rays. A photographic plate was laid film side down on one piece of metal with a second piece of metal above the plate so that the areas of contact of metal and plate overlapped. When exposed to Roentgen rays from above and developed the plate was much less dense where the two pieces of metal overlapped than where the plate was in contact with the upper piece of metal alone. The plate was densest where in contact with the metal below alone. Mr. Gorton found this effect with Ag, Au and Cu, but not with Pb.

An arrangement similar to that described by Mr. Gorton was tried by the writer with Ag, Pb, Fe, Cu and other metals and in every case the effect found by him in the case of Ag was observed. In an attempt to find an explanation for this effect, further experiments were carried out as described below.

Exposures were made from above with the plate face down, part of the plate being in contact with a piece of metal below the plate and part protected by a piece of metal a few millimeters below the plate. The second piece of metal was found to produce nearly the same effect as the first. In fact it was found that nearly as much effect was obtained when there was no metal directly behind the plate if only the plate was protected from a general scattered radiation from below. Thus a plate which was exposed with face down on the end of an iron tube four or five inches long showed 18 per cent. more light transmission through the portion over the inside of the tube than through the portion outside the tube, while the portion in contact with the iron was darkest of all. Plates exposed through an opening in a lead screen which would prevent a general scattered radiation from behind were in almost every case darker over the metal.

These experiments indicate two effects from metal behind the plate; first a protection of the plate from a scattered radiation originating in the region behind the plate; second, the production of a secondary radiation in the metal itself which counteracts this protective effect, the ratio between the general secondary radiation and the radiation from the metal itself determining which effect will predominate. These two effects together explain the phenomenon as originally observed.

The next step was to compare the effects from different metals with primary rays of various penetrations. First exposures were made with strips of Pb, Fe, and Cu under the plate and similar strips laid at right angles to these above the plate. At tube voltages from 55 to 90 K. V. the plate was lightest over the Fe and darker over the Cu and Pb in order without regard to the metal above. A series of exposures were next made with strips of different metals behind the plate, the plate being exposed behind an opening in a lead screen. At 90 K. V. tube voltage the darkening was in this order, Ag most, Pb, Fe, Al, one plate for instance giving the following values of relative transmission; over Ag 75, Pb 92, Fe 94, Al 100. At 55 K. V. and 35 K. V. the order was the same, one plate at 35 K. V. giving the following values of relative transmission; over Ag 85, Pb 89, Fe 95, Al 100. At 25 K. V. the order was changed, a typical plate giving these values; Pb 83, Fe 84, Ag 89, Al 100. At 17 K. V. and 14 K. V. the Ag gives very much less darkening and the Fe much more. For instance a typical plate at 14 K. V. gave these values: Zn 39, Cu 55, Fe 61, Pb 63, Ag 80. At all voltages tried Zn, Cu and Fe produced darkening in the order named.

These results may be explained from the relative abilities of the metals to emit secondary radiation under excitation by primary rays of different penetrations. The curves in Fig. 1 are drawn from data given by Sadler,[1] and by Whiddington and Kaye,[2] to show the relative secondary emission efficiencies of these metals for primary radiations corresponding to different tube voltages. The curve for Al is not shown as it would be a

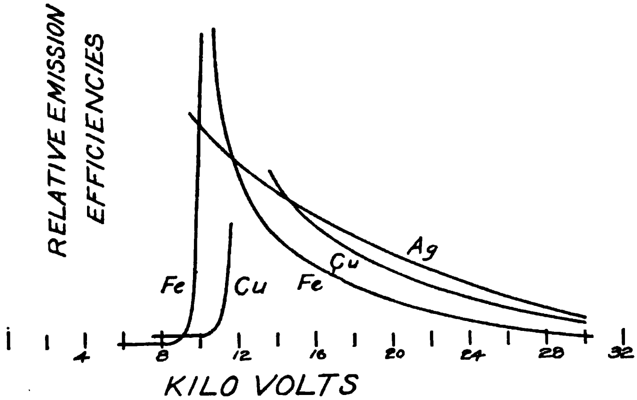

Fig. 1.

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[1] Phil. Mag., 22: 541.

[2] Kaye's X-Rays, p. 127.

nearly straight line lying very close to the axis, corresponding to very low emission efficiency at all voltages and consequently very slight darkening effect. The curves explain the order of darkening from Fe, Cu and by analogy that from Zn. The fact that silver produced relatively slight darkening at low voltages may perhaps be explained from the fact that the absorption coefficient of the silver of the emulsion is very much greater for the characteristic radiation from the Fe, Cu and Zu than for the scattered radiation from the Ag. However the darkening effect even from the silver was greatly reduced by interposing a single thickness of paper between the metal and the plate, which would seem to indicate that much of the darkening effect was produced by a corpuscular radiation, easily absorbed. The explanation of the sudden increase in the darkening from the silver at about 25 K. V. is undoubtedly that the characteristic radiation of silver was excited at that voltage, the total amount of secondary radiation from silver being thereby greatly increased.

The effects observed are interesting in connection with the suggested use of a metal behind the plate as an intensifying screen. Figs. 2 and 3 show some results obtained when using as object a paraffine block made in the form of steps 1 cm. high. The curves show the relative light transmission through different parts of the plates under successive thicknesses of paraffine with and without metal behind.

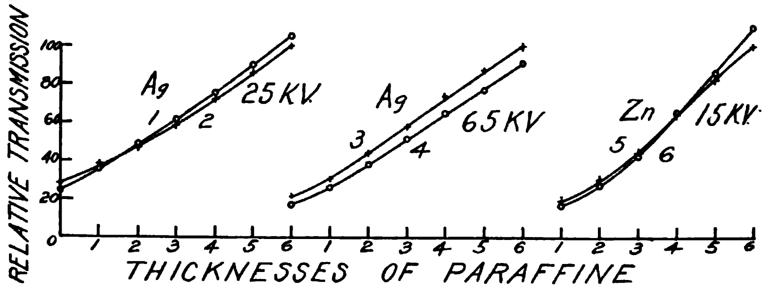

Fig. 2.

Curves with circles are with metal backing. Curves with crosses are without metal backing.

The plate from which the values for Curves 3 and 4 were obtained was exposed through an opening in a lead screen; in exposing the other plates no attempt was made to reduce the scattered radiation from behind. The values for curves 11 and 12 were obtained from a plate exposed behind successive thicknesses of sheet iron instead of paraffine. Curves 3 and 4 indicate for a particular case the amount of intensification obtained. Although marked in many cases this effect can hardly be compared to that obtained with a regular intensifying screen.

The most noticeable effect is shown by the other curves. In these the steeper slope indicates a better contrast in the portion of the plate backed by the metal. This was also shown in a plate exposed under a block of paraffine on which were laid objects of varying thickness. The relative darkening under corresponding parts where the plate was backed by metal and where unprotected is shown by the relative transmissions. This improvement in the contrast of the plate is to be expected as a result of preventing the fog due to secondary scattered radiation. These plates were exposed under varying conditions so that the results obtained can not be taken as typical for the metals used.

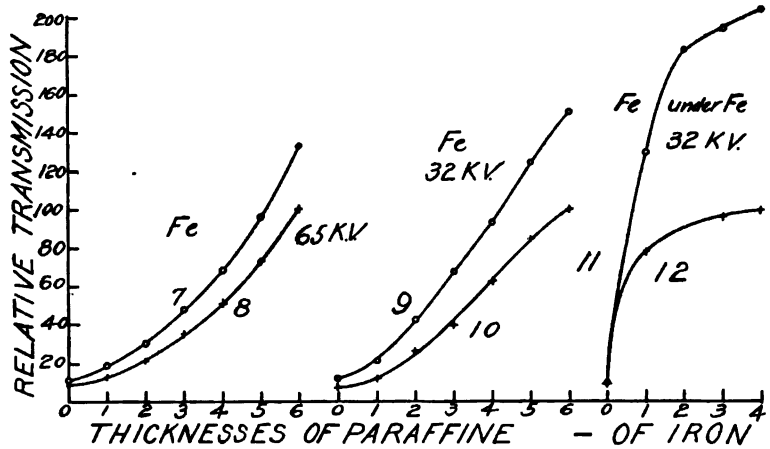

Fig. 3.

Curves with circles are with metal backing. Curves with crosses are without metal backing.

	Metal Backed.	Unprotected.
Glass tube	21	20
	36	31
	32	28
Rubber tube	20.5	19
	24	21.5
	23.5	21
Rubber tube	33	24.5
	26	21.5
	2	3
Metal	35	32.5
	80	68
	78	67

These last results show plainly the advantage to be obtained from a reduction of the amount of scattered radiation originating behind the plate. If the amount of this is sufficiently reduced the use of metal behind the plate becomes of relatively small advantage at best. But if provision is not made for reducing this scattered radiation from behind the plate the use of metal backing results in much better contrast.

It is also evident that a sensitive plate in the neighborhod of an active Roentgen ray tube should be entirely surrounded by lead and not merely screened from the direct radiation from the tube.

A mechanically rectified high-tension alternating current was used for operating the tube. The voltage was measured by means of a Siemens-Halske attracted disk type voltmeter. The values of voltage used were obtained by multiplying the voltmeter readings by 1.4 to give the peak values of the voltage.

SUMMARY.

1. An explanation is given for a peculiar effect from secondary Roentgen radiation, originally noted by F. R. Gorton.

2. The relative intensifying effect from different metals placed behind a plate when exposed to Roentgen rays of various penetrations has been investigated.

3. Additional evidence is given of the need for preventing or screening off the general scattered radiation.

I wish to acknowledge the suggestions and assistance given me by Professor J. S. Shearer.

PHYSICAL LABORATORY,
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A NEW HYDROMETER OF TOTAL IMMERSION WITH ELECTRO-MAGNETIC COMPENSATION.

By Anders Ångström.

In the present note, I intend to propose a new method for determining the specific gravity of liquids and especially the specific gravity of seawater, from which the salinity may be calculated with high degree of accuracy.

The different hydrometers which have been used or merely suggested for this kind of work may be divided into two groups: floating hydrometers and such as are worked by some method of total immersion. As regards the floating hydrometers, it may be mentioned that Nansen has made a very careful study of the errors and irregularities adhering to these instruments. Nansen arrives at the conclusion that the chief cause of their drawbacks lies in uncontrollable changes in the surface-tension of the water; he also discusses the precautions and corrections that are necessary in order to eliminate these influences. The number of the precautions to take is however so large, that several eminent oceanographers are inclined to discard the floating hydrometer as unsuitable for accurate work.

In order to avoid the errors arising from variations in the surface tension of the liquid, hydrometers of *total immersion* have been invented; and here I may refer to the papers of Guglielmo, of Reggiani and especially to the discussion presented by Nansen, who gives several references regarding this subject. It appears that the methods of total immersion are primarily of two kinds: such methods, where the hydrometer itself through the adding of small loads is brought to the point where it just sinks down totally in the liquid, and such ones where the specific gravity of the liquid is changed, in order to attain the same end. The ingenious method used by Nansen is a combination of these two principles. Very small changes in the density can be produced by raising or lowering the temperature of the liquid by means of a thin platinum spiral, heated by an electric current.

The objections against these methods, that, when properly used, seem to be very accurate, arise from the inconvenience of loading and unloading the hydrometer, or, if the heating method is used, from the difficulty of knowing if the hydrometer and the air contained in it have reached the temperature of the surroundings or not. And finally the hydrometer must then be adjusted to an unstable equilibrium, as the least change will bring the hydrometer to the surface or to the bottom of the vessel. A considerable time is therefore required for each determination.

A third and indirect, very accurate, method is that of determining by titration the amount of chlorine contained in the seawater. This method is almost exclusively used by the international organization for the study of the North Sea. From the amount of chlorine in the water, its salinity as well as its density at different temperatures can be found from Knudsen's well-known hydrographic tables.

While I was engaged in certain investigations at Bornö Station, its director, Professor Otto Pettersson called my attention to the want of an improved method of total immersion more convenient than those described above, and as accurate as the chemical method. It then occurred to me that considerable advantage might be gained with a hydrometer of total immersion worked by electromagnetic compensation, *i. e.*, counterbalancing the buoyancy of a float completely immersed in seawater by an electromagnetic force acting on a piece of soft iron within the float.

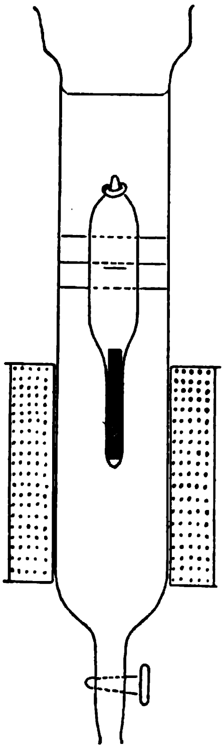

Fig. 1.

The instrument constructed according to this idea is shown in Fig. 1. The float is drawn out into a narrow tube, that contains a rod of soft iron, 4 cm. in length, and some 3 mm. wide. The outer vessel, which contains the liquid to be investigated, has its lower part drawn out to the shape shown by the figure. It is surrounded by a coil, that has a length of about 12 cm. If the force acting on a piece of soft iron, which varies both with the intensity and the divergency of the E.M. field, is plotted against the vertical distance from the center of the coil (C), we would obtain a curve of the general type shown in Fig. 2. Suppose now that the electromagnetic force is counterbalanced by the buoyancy of the float, containing the piece of soft iron. The float will then come to rest in a position, where the E.M. force is equal to its buoyancy. The equilibrium is stable provided that the float is brought to rest at a place corresponding to a certain point (P) on the part AC of the curve. An increase of the current through the coil or a decrease of the buoyancy of the float, viz., the specific gravity of the liquid, will bring the float nearer to the center (*A*). If the float is always brought to rest at a fixed distance from the center, a certain current through the coil will always correspond to the same buoyancy. The adjustment is very sensitive at points corresponding to the maximum of the curve, where dl/df has its largest value.

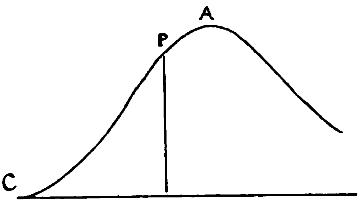

Fig. 2.

A determination is made in the following way. The water sample is poured into the vessel which has previously been washed out with another part of the same sample. The float is loaded with a fine platinum spiral of known weight until it very nearly sinks in the liquid. By sending a current through the coil the float is depressed until the mark etched on the float coincides with that on the wall of the envelop. The current is measured on a milliammeter and from the observed value the specific gravity of the water sample can be found from an empirical table obtained by standardizing the instrument once for all with a few samples of different salinities checked through titrations. The final adjustment is made by the E.M. compensation. The rough adjustment is realized by loading the float with a set of light platinum spirals of known weight. In this way the use of the instrument can be extended over the whole range of specific gravity occurring in oceanographic research, *i. e.*, 1.000 to 1.028, whereas the sensibility can nevertheless be kept as high as 0.00004 or even higher. This sensibility allows of measuring the salinity of a water sample with the degree of accuracy agreed upon as sufficient for modern research at the International Congress of Stockholm, 1899.

I may finally include here some observations made with a preliminary type of the described instrument. The load of the float was adjusted until the float was just nearly sinking in a water sample of a specific gravity corresponding to a salinity of about 23.4 pro mille. Varying the salinity, I must send currents of varying strength through the coil, in order to keep the float at the mark. With the aid of a current between 0 and 75 milliamperes, I may then control a range corresponding to a difference of salinity of about 2 pro mille. In Fig. 3 the relation between the current (y) and the corresponding salinity (x) is given by a curve. The observations are represented by circles. The permeability of the iron not being constant, the relation is evidently not a linear one. But if we confine ourselves to work with fields that are not too small, viz., with currents larger than 35 milliamperes for the special kind of instrument here used, the relation may practically be regarded as linear. It must however be noticed that the sensitiveness of the instrument is larger the less the current is and it may therefore sometimes be found favorable to work with small currents, which always can be attained through extending the use of loads. The mean deviation of the observations from the curve corresponds to less than 0.01 per cent. of salinity. The method may naturally be applied with advantage in all cases where the specific gravity of liquids is to be determined with high degree of accuracy, within relatively small intervals.

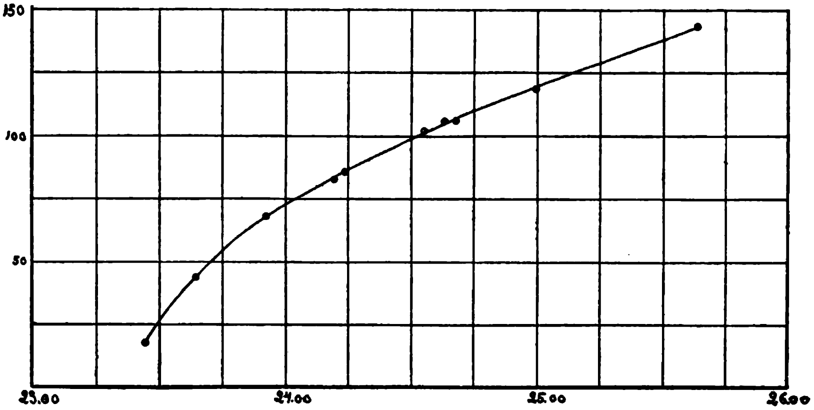

Fig. 3.

The Ordinates give currents used for compensation. The Abscissas represent satinity of water sample, given in pro mille.

BORNÖ STATION, SWEDEN,
December, 1914.

SIGNAL PROPAGATION IN DISPERSIVE MEDIA.

By Walter Colby.

In a recent paper[1] Prof. Sommerfeld has discussed a problem originally suggested by the relativity theory, viz., Can a signal be transmitted in a dispersive medium with a velocity greater than that of light in vacuum. One is naturally led to this question when he considers that in the case of anomalous dispersion where the value of the index of refraction may be less than unity, the actual rate of progress of a given wave crest, in a monochromatic wave train does exceed its velocity in vacuum. The solution of the problem, however, does not follow straightway, for a signal must differ from a monochromatic wave train in that it has some fiducial mark, some irregularity in form, a beginning or an end by means of which one identifies it at the detector. And in this irregularity one necessarily introduces new frequencies. A monochromatic wave train cannot therefore be used for this problem. Professor Sommerfeld has taken as the simplest form of signal a sine wave of constant amplitude beginning at a given moment and persisting thereafter. The cessation of such a wave train would not differ from the superposition of a precisely similar disturbance in opposite phase. A more complicated signal could likewise be reduced by analysis to a series of simple waves of the above type and would therefore add nothing to the generality of the result. The rather surprising conclusion of the paper cited above is that although the rate of progress of the signal-front cannot exceed vacuum velocity even at an absorption band, it cannot fall below it in the remaining regions. To be sure, the amount of energy which reaches the new point at the first instant is too small to affect any known detector and to measure the signal velocity by it or to speak of this extremely small disturbance as the signal may be questionable. In the same number of the Annalen, L. Brillouin[2] has defined the arrival of the signal as that moment at which the disturbance reaches the order of magnitude of its final value. He also identifies signal velocity with group velocity except in the region of anomalous dispersion where this term loses its meaning.

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[1] Ann. d. Phys., 44, p. 177, 1914.

[2] Ann. d. Phys., 44, p. 203, 1914.

The problem naturally extends itself to an investigation of the changes of form which such a "signal front" may experience at the boundary of a dispersive medium. As Professor Sommerfeld has pointed out, since rectilinear propagation acquires the characteristics of the medium only gradually, one may readily expect the wave to suffer a similar initial change on refraction and reflection.

In the present paper I have undertaken an investigation of the changes experienced by a signal at a plane boundary surface both with reference to its form and direction of propagation, also a brief discussion of the reflected wave. The method used by Sommerfeld has been adapted with very slight variation to the first part of this problem.

Let us consider the signal as existing only between the time limits $t = 0$ and $t = T$, and having the form

$$\begin{aligned} f(t) &= 0 &\quad &\text{for} \quad t < 0, \\ f(t) &= \sin\frac{2\pi t}{\tau} &\quad &\text{for} \quad 0 < t < T, \\ f(t) &= 0 &\quad &\text{for} \quad t > T. \end{aligned}$$

Putting this in the form of a Fourier integral we have

$$f(t) = \frac{1}{\pi}\int_0^\infty dn \int_0^T \sin\frac{2\pi\alpha}{\tau}\cos n(t-\alpha)d\alpha$$

If T, the duration of the signal, be large in comparison with τ, the period of vibration of the incident light, we may without loss of generality set $T = N\tau$, where N is an integer. Performing the integration with respect to the variable α we obtain

$$f(t) = \frac{2}{\tau}\int_0^\infty \frac{dn}{n^2 - \left(\frac{2\pi}{\tau}\right)^2}(\cos n(t-T) - \cos nt).$$

Or in the exponential form

$$f(t) = \text{Real part of } \frac{1}{\tau}\int \frac{dn}{n^2 - \left(\frac{2\pi}{\tau}\right)^2}(e^{-in(t-T)} - e^{-int}).$$

The complex integral has the great advantage that the two terms may be treated separately and the points ($n = \pm 2\pi/\tau$) avoided by a deformation of the integration path in the complex n plane. In the real integral these points present convergence difficulties unless the whole integrand be treated together. Moreover a separation of the terms is highly desirable for, as we see by inspection, one represents the setting-in of the signal and the other its cessation. In fact, in the following work, it is only necessary to consider the "front" of the signal as is done in

Sommerfeld's paper, whereby our integral reduces to

$$(1)\qquad f(t)=\frac{1}{\tau}\int_{+\infty}^{-\infty}\frac{dn}{n^2-\left(\frac{2\pi}{\tau}\right)^2}e^{-int},$$

where the integration path extends from $+\infty$ to $-\infty$ along the real axis with deformations about the poles $\pm(2\pi/\tau)$. Let us now consider the surface of separation of the vacuum and the dispersive medium as the plane $x=0$. If the wave be incident at an angle θ, the integral in medium one ($x<0$) has the form

$$(2)\qquad \frac{1}{\tau}\int_{+\infty}^{-\infty}\frac{dn}{n^2-\left(\frac{2\pi}{\tau}\right)^2}e^{-in\left(t-\frac{x\cos\theta+y\sin\theta}{c}\right)}.$$

For the second medium the amplitude is altered with the help of the Fresnel formulas. If the above integral represents either component of the electric vector then we may use the factors

$$D_p=\frac{2}{\mu+\frac{\cos\varphi}{\cos\theta}}=\frac{2\mu\cos\theta}{\mu^2\cos\theta+\sqrt{\mu^2-\sin^2\theta}},$$

$$D_s=\frac{2}{1+\mu\frac{\cos\varphi}{\cos\theta}}=\frac{2\cos\theta}{\cos\theta+\sqrt{\mu^2-\sin^2\theta}}$$

respectively for the two components, where

$$\mu^2=1+\frac{a^2}{n_0^2+2ipn-n^2},$$

$$a^2=\frac{Ne^2}{m}.$$

N, e, m, n_0 and p denoting respectively the number of resonators per c.c., their electric charge, mass, natural vibration frequency multiplied by 2π, and damping constant.

The corresponding alteration for the exponential factor may be deduced from the following considerations. Let us assume the form to be $e^{i(\alpha x+\beta y-nt)}$. Now since the loci of equal amplitudes are planes parallel to the surface $x=0$, the coefficient of y must be $\beta=(n\sin\theta)/c$ as before. If we denote by φ the complex angle of refraction then $\alpha/\beta=\cot\varphi$, $\alpha=\beta\cot\varphi=n/c\sin\theta\cot\varphi$. Since $\mu=\sin\theta/\sin\varphi$, then $\sin\theta\cot\varphi=\sqrt{\mu^2-\sin^2\theta}$, and $\alpha=n/c\sqrt{\mu^2-\sin^2\theta}$. The total integral for the component of the electric vector normal to the plane of incidence, for $x>0$, is therefore

$$(3)\quad f(t, x, y) = \frac{1}{\tau}\int \frac{2\cos\theta}{\cos\theta + \sqrt{\mu^2 - \sin^2\theta}}\, e^{-in\left(t - \frac{x\sqrt{\mu^2 - \sin^2\theta} + y\sin\theta}{c}\right)} \frac{dn}{n^2 - \left(\frac{2\pi}{\tau}\right)^2}$$

Our problem now reduces itself to the evaluation of integral (3). If we consider the n complex plane we note again the poles on the real axis at $\pm\, 2\pi/\tau$, also branch cuts occasioned by the square root $\sqrt{\mu^2 - \sin^2\theta}$. Locating the branch points by setting $\sqrt{\mu^2 - \sin^2\theta}$ equal successively to 0 and ∞ we find them to lie at

$$U = -\rho \pm \sqrt{n_0^2 - \rho^2 + \frac{a^2}{1 - \sin^2\theta}},$$

$$N = -i\rho \pm \sqrt{n_0^2 - \rho^2}.$$

The branch cuts may therefore be drawn (Fig. 1) parallel to the real axis in the lower half plane and symmetrically placed with respect to the imaginary axis. The inner points are fixed by the properties of the medium but the outer ones depend also on the obliquity of the ray.

Let us turn again to the question of the integration path which, for the original integral, was along the real axis. One may convince himself that, for the exponential form here chosen, the deformation of the integration path about the real poles must be made in the upper half plane, by an integration of expression (1) to which (3) reduces for the point $x = y = 0$. If the integration path be correctly chosen, the result of this integration should be the original form of disturbance assumed. Rewriting integral (1)

$$f(t) = \frac{1}{\tau}\int \frac{dn}{n^2 - \left(\frac{2\pi}{\tau}\right)^2} e^{-int}.$$

We note that if we set $n = a + ib$, we have as a factor e^{bt} which causes the integrand to vanish for $t < o$ and b very large. Therefore if we deform the integration path upwards we see that the integral vanishes for $t < o$. Deforming downwards a similar result would be obtained for $t > o$, were it not for the circuits hanging about the poles $\pm\, (2\pi/\tau)$. These may be evaluated by Cauchy's theorem of residues with the result

$$\frac{2\pi i}{\tau}\left[\frac{e^{-int}}{n - \frac{2\pi}{\tau}}\right]_{n=-\frac{2\pi}{\tau}} + \frac{2\pi i}{\tau}\left[\frac{e^{-int}}{n + \frac{2\pi}{\tau}}\right]_{n:\frac{2\pi}{\tau}} = \frac{1}{2}\left(e^{-\frac{2\pi t}{\tau}} - e^{\frac{2\pi t}{\tau}}\right) = \sin\frac{2\pi t}{\tau}.$$

The result is therefore

$$f(t) = 0 \qquad \text{for} \quad t < o.$$

$$f(t) = \sin\frac{2\pi t}{\tau} \quad \text{for} \quad t > o \text{ as assumed.}$$

Turning now to Integral (3) and deforming the path upward to large positive imaginary values of n, μ becomes equal to unity and the integral simplifies to

$$\frac{1}{\tau}\int e^{-in\left(t-\frac{x\cos\theta+y\sin\theta}{c}\right)}\frac{dn}{n^2-\left(\frac{2\pi}{\tau}\right)^2}.$$

We have already found that this form of integral vanishes when the factor of $-in$ in the exponential part has a negative sign, that is, when

$$t<\frac{x\cos\theta+y\sin\theta}{c}.$$

Here we see as in Prof. Sommerfeld's paper that no disturbance can reach the point whose coördinates are x, y in less time than $(x\cos\theta+y\sin\theta)/c$, *i. e.*, more quickly than the light could traverse the intervening distance in vacuum. The possibility of more rapid propagation in the case of anomalous dispersion is thus excluded.

For values of t greater than the one defined above, the integral will vanish in the region where n has a large negative imaginary part. If we deform the path downwards, however, circuits are left about the poles and branch cuts. The position of the branch cuts in the complex plane leads us to expect in the result an exponential factor vanishing with increasing time whereas the integration about the real poles will be free from it. The former then will represent the free and the latter the forced vibrations. The integration about the branch cuts cannot be further evaluated but we may use Cauchy's theorem again for the calculation of the forced vibrations with the result

$$\frac{2\pi i}{\tau}\left\{\frac{2\cos\theta}{\cos\theta+\sqrt{\mu^2-\sin^2\theta}}\frac{e^{-in\left(t-\frac{x\sqrt{\mu^2-\sin^2\theta}+y\sin\theta}{c}\right)}}{n+\frac{2\pi}{\tau}}\right\}_{n=\frac{2\pi}{\tau}}$$

$$+\frac{2\pi i}{\tau}\left\{\frac{2\cos\theta}{\cos\theta+\sqrt{\mu^2-\sin^2\theta}}\frac{e^{-in\left(t-\frac{x\sqrt{\mu^2-\sin^2\theta}+y\sin\theta}{c}\right)}}{n-\frac{2\pi}{\tau}}\right\}_{n=-\frac{2\pi}{\tau}}.$$

Changing the sign of n in μ^2 only affects its imaginary part giving the conjugate value. If then we set $\sqrt{\mu_+^2-\sin^2\theta}=\alpha+i\beta$ and $\sqrt{\mu_-^2-\sin^2\theta}=\alpha-i\beta$ where μ_+^2, μ_-^2 are the values taken by μ^2 when $n=\pm 2\pi/\tau$ respectively, the two terms in our result may be combined. Taking then the real part we have

$$\frac{2\cos}{(\alpha+\cos\theta)+\beta^2}e^{-\frac{2\pi}{c\tau}\beta x}\left\{(\alpha+\cos\theta)\sin\frac{2\pi}{\tau}\left(t-\frac{\alpha x}{c}-\frac{y\sin\theta}{c}\right)\right.$$
$$\left.+\beta\cos\frac{2\pi}{\tau}\left(t-\frac{\alpha x}{c}\frac{y\sin\theta}{c}\right)\right\}.$$

The exponential factor contains x but not t. This is therefore a part of the whole disturbance which does not decrease as time goes on but whose amplitude diminishes the deeper it penetrates the second medium. For large values of t it represents the complete disturbance. A calculation of the forced vibration for the component of the electric field parallel to the plane of incidence gives a similar expression. The change of phase at the boundary as indicated by the coefficients of the sine and cosine terms is a different one for the two components, showing the familiar change in state of polarization on refraction.

For an investigation of the integral for smaller values of t, we may proceed most simply by restricting ourselves to regions not in the neighborhood of an absorption band, whereby $2\pi/\tau \neq n_0$ and ρ may be taken vanishingly small. This enables us to develop the expression $\sqrt{\mu^2-\sin^2\theta}$ as a power series and integrate straightforwardly. We may very conveniently change the variable by setting

$$n = m\frac{2\pi}{\tau} \quad \text{and} \quad n_0 = m_0\frac{2\pi}{\tau}.$$

Then

$$\sqrt{\mu^2-\sin^2\theta} = \sqrt{1+\frac{a^2}{m_0^2-m^2}\left(\frac{\tau}{2\pi}\right)^2-\sin^2\theta}$$

and

$$dn = dm\cdot\frac{2\pi}{\tau}.$$

If we also write

$$K = m\frac{2\pi}{c\tau}\left\{\sqrt{1+\frac{a^2}{m_0^2-m^2}\left(\frac{\tau}{2\pi}\right)^2-\sin^2\theta}-\cos\theta\right\}$$

and

$$t' = t-\frac{x\cos\theta+y\sin\theta}{c}.$$

Integral (3) becomes

$$(4)\qquad \frac{1}{2\pi}\int_{\infty}^{-\infty}\frac{2dm}{1+\sqrt{1+\frac{a^2}{m_0^2-m^2}\left(\frac{\tau}{2\pi}\right)^2-\sin^2\theta}}\,\frac{e^{ikx-im\frac{2\pi t'}{\tau}}}{m^2-1}.$$

Let us now develop the integrand as a descending power series valid for large values of m.

$$\left\{1-\left[\frac{a^2}{m^2-m_0^2}\frac{\tau^2}{4\pi^2}+\sin^2\theta\right]\right\}^{\frac{1}{2}}$$

may be put in the form

$$\cos\theta - \frac{a^2\tau^2}{8\pi^2}\left\{\frac{\varphi_1}{m^2} + \frac{\varphi_2}{m^4} + \cdots\right\},$$

where φ_n is a polynomial easily evaluated for the lower orders.

$$Kx = -\frac{a^2\tau x}{4\pi c}\left\{\frac{\varphi_1}{m} + \frac{\varphi_2}{m^3} + \frac{\varphi_2}{m^5} + \cdots\right\} = -\xi\left\{\frac{\varphi_1}{m} + \frac{\varphi_2}{m^3} + \cdots\right\}$$

where

$$\xi = \frac{a^2\tau x}{4\pi c}.$$

Substituting in $e^{ikx}/(m^2 - 1)$ and collecting terms we have

$$\sum_{\nu=0}^{\infty}\frac{1}{m^{\nu+2}}\frac{(-i\varphi_1\xi)^\nu}{\nu!} + \left\{1 + \varphi_1\left(\frac{-i\xi}{m}\right)\right\}\sum_{0}^{\infty}\frac{1}{m^{\nu+4}}\frac{(-i\xi\varphi_1)^\nu}{\nu!} + \cdots$$

The amplitude $(2\cos\theta)/(\cos\theta + \sqrt{\mu^2 - \sin^2\theta})$ gives when developed

$$1 + \frac{\alpha^2}{4}\frac{1}{m^2} + \left\{\frac{\alpha^2}{8} + \frac{\alpha}{4}m_0{}^2\right\}\frac{1}{m^4} + \cdots$$

where

$$\alpha = \frac{a^2\tau^2}{4\pi^2\cos^2\theta}.$$

The total integrand may then be written

$$\left[\Sigma\frac{1}{m^{\nu+2}}\frac{(-i\xi\varphi_1)^\nu}{\nu!} + \left\{\frac{\alpha}{4} + 1 + \frac{(-i\xi\varphi_1)}{m}\right\}\Sigma\frac{1}{m^{\nu+4}}\frac{(-i\xi\varphi_1)^\nu}{\nu!} + \cdots\right]e^{-im\frac{2\pi t'}{\tau}}$$

The singularities consist now of poles at the origin. Since the integral still vanishes where m has a large negative imaginary part we may replace our integration path across the upper half plane by a circle of infinite radius with its center at the origin. Applying again the Cauchy theorem we obtain for the first term

$$\frac{1}{2\pi}\sum_{0}^{\infty}\left(\frac{-i\xi\varphi_1}{\nu!}\right)^\nu\int e^{-im\frac{2\pi t'}{\tau}}\frac{dm}{m^{\nu+2}} = \frac{1}{2\pi}\sum_{0}^{\infty}\left(\frac{-i\xi\varphi_1}{\nu!}\right)^\nu\frac{2\pi i}{(\nu+1)!}\left(\frac{-2\pi i t'}{\tau}\right)^{\nu+1}$$

$$= \frac{2\pi t'}{\tau}\sum_{0}^{\infty}\frac{\left(\dfrac{-2\pi\xi t'\varphi_1}{\tau}\right)}{\nu!\,(\nu+1)!}.$$

By comparison with the general expression for Bessel's function of the nth order

$$J_n(x) = \left(\frac{x}{2}\right)^n\sum_{0}^{\infty}\frac{\left(\dfrac{-x^2}{4}\right)^\nu}{\nu!\,(\nu+n)!}.$$

We may write the above result

$$\sqrt{\frac{2\pi t'}{\tau\xi\varphi_1}}\,J_1\left(2\sqrt{\frac{2\pi\xi\varphi_1 t'}{\tau}}\right).$$

Later terms give Bessel's functions of higher orders but with the same argument. Omitting the arguments we have for the complete result

$$\sqrt{\frac{2\pi t'}{\tau\xi\varphi_1}}J_1 - \left(\frac{\alpha}{4} + 1\right)\left(\frac{2\pi t'}{\tau\xi\varphi_1}\right)^{\frac{3}{2}}J_3 + \varphi_1\xi\left(\frac{2\pi t'}{\tau\xi\varphi_1}\right)^{\frac{4}{2}}J_4 + \cdots.$$

For very small values of t' the first term exceeds the others in order of magnitude. This is assured not only by the increasing order of t'/ξ but also by the Bessel's functions themselves which vanish at the origin as powers which grow with the order. It will be noted that boundary effects are limited to those terms which contain α. If therefore we set $\theta = 0$ in the first term it should give us Sommerfeld's result. $\varphi_1 = 1/\cos\theta = 1$ for $\theta = 0$. We have therefore for the first forerunners in the case of normal incidence

$$\sqrt{\frac{2\pi t'}{\tau\xi}}J_1\left(2\sqrt{\frac{2\pi\xi t'}{\tau}}\right).$$

This form of the result has been fully discussed in the Sommerfeld paper and plotted as an approximate sine wave with increasing amplitude and period. Obliquity at the boundary has therefore an effect of decreasing the amplitude and period of these early forerunners. The next term in the series to appear with increasing t' is the third (due to the factor ξ). If we use as numerical values of the constants

$$m_0 = 10,\ \tau = 1.6\cdot 10^{-15},\ \xi = 7.8\cdot 10^{6}$$

also

$$\theta = 0,\ \varphi_1 = 1,\ \alpha = 125$$

whereby the time between the first two maxima is $4\cdot 10^{-22}$ sec. we find the third term of our series attains the magnitude of the first when t' has the order of magnitude of 10^{-14}, that is, many periods after the theoretical beginning of the disturbance.

DIRECTION OF THE RAY.

For the study of the deviation of the signal ray it is much more convenient to think of the total electric vector of the incident beam as parallel to one of the coördinate axes. Let us again take the plane $z = 0$ as the plane of incidence and consider the electric vector as perpendicular to it. Integral (3) may again be taken to represent this quantity but for brevity we shall denote it by the symbol

$$\int \Phi dn = Z.$$

For the other two components we have necessarily

$$X = Y = 0.$$

To deduce the values of the components of the magnetic vector, we may use the Maxwell equations

$$-\frac{1}{c}\frac{\partial H}{\partial t} = \operatorname{curl} E.$$

Denoting the x component by α, we have

$$-\frac{1}{c}\frac{\partial \alpha}{\partial t} = \frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z}, \quad \frac{\partial \alpha}{\partial t} = -\frac{1}{\tau}\int in \sin\theta\Phi dn$$

$$\alpha = -\frac{1}{\tau}\int\int in \sin\theta\Phi dn\, dt = \frac{1}{\tau}\sin\theta\int\Phi dn.$$

Similarly

$$\beta = -\frac{1}{\tau}\int\sqrt{\mu^2 - \sin^2\theta}\Phi dn$$

$$\gamma = 0.$$

We are now ready to build up the vector product of the electric and magnetic fields and form the Poynting vector. For the three components we obtain

$$S_x = \frac{c}{4\pi}(\gamma Y - \beta Z) = \frac{c}{4\pi\tau^2}\int\sqrt{\mu^2 - \sin^2\theta}\Phi dn\int\Phi dn,$$

$$S_y = \frac{c}{4\pi}(\alpha Z - \gamma X) = \frac{c}{4\pi\tau^2}\sin\theta\int\Phi dn\int\Phi dn,$$

$$S_z = \frac{c}{4\pi}(\beta X - \alpha Y) = 0.$$

If we now denote the angle of refraction by δ we may write

$$\cot\delta = \frac{S_x}{S_y} = \frac{\int\sqrt{\mu^2 - \sin^2\theta}\Phi dn}{\sin\theta\int\Phi dn}.$$

We are interested here only in the initial direction of the ray and must seek an evaluation of this expression for values of t' slightly greater than zero. Obviously the method last employed will serve here also. We have already obtained developments for the factors in the integrand of the numerator. Multiplying we obtain

$$\sqrt{\mu^2 - \sin^2\theta}\Phi dn = \cos\theta\int\Phi dn$$
$$-\frac{1}{2\pi}\int\frac{a^2\tau^2\varphi_1}{8\pi^2}e^{-im\frac{2\pi t'}{\tau}}\sum_0^\infty\frac{1}{m^{\nu+4}}\frac{(-i\xi\varphi_1)^\nu}{\nu!} + \cdots.$$

Integrating as before

$$= \cos\theta\int\Phi dn + \frac{a^2\tau^2}{8\pi^2}\varphi_1\left(\frac{2\pi t'}{\tau\xi\varphi_1}\right)^{\frac{3}{2}} J_3\left(2\sqrt{\frac{2\pi\xi\varphi_1 t'}{\tau}}\right) + \cdots.$$

Here again we have a series which for small values of t' does not differ in value from its first term. Dividing by $\sin\theta\int\Phi dn$ we find likewise for vanishingly small values of t'

$$\cot\delta = \frac{\cos\theta}{\sin\theta} = \cot\theta, \quad \delta = \theta.$$

In other words *the initial front of the wave train which penetrates the dispersive medium with the velocity of light in vacuum, suffers no deviation at the boundary.* As t' grows we must consider later terms in the series solution. Suppose for a first approximation we neglect terms later than the first in the series solution of the denominator. Dividing the complete numerator we then obtain

$$\cot\delta = \cot\theta + \frac{ct'}{x\sin\theta}\frac{J_3}{J_1} + \frac{8\pi^2c^2t'^2}{a^2\tau^2x^2\varphi_1^2\sin\theta}\left(\frac{\alpha^2}{4}\varphi_1 + \varphi_1 + \varphi_2\right)\frac{J_5}{J_1} + \cdots.$$

The ratio J_n/J_1 equals zero for zero argument ($n > 1$) and grows slowly at first with increasing argument. Its value also decreases with rising order of the numerator for small values of the argument. So the ray suffers no deviation until t' attains a sufficiently high value for the second term to be comparable with the first. All factors of this term are essentially positive for values of the argument less than 3.83 +, the value of the first root of J_1. Cot δ will therefore increase from the original value cot θ with increasing t', *i. e.*, δ will become smaller, the ray will be bent continuously toward the normal. The terms succeeding the first appear here much more rapidly then in the series just discussed as one may see

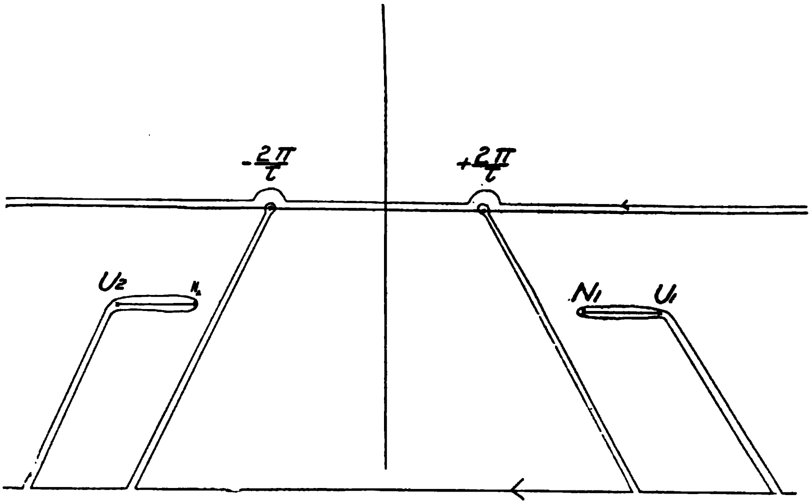

Fig. 1.

by calculating the magnitude of the factor of t' J_3/J_1. For $\sin\theta = 1/10$, $x = 1$ it becomes 3.10^{11}. The factor of t' J_5/J_1 for the same angle rises to the magnitude of 10^{22}. That these terms do appear in the above mentioned order is assured by the increasing power of t' and the increasing order of J_n in the numerator.

The Reflected Ray.

To build up an integral for the reflected ray is a much simpler task. The exponential part retains the form of integral (2) except for sign. There remains only to alter the amplitude by the Fresnel formula and we have for the component normal to the plane of incidence

$$(5) \qquad \frac{1}{\tau}\int \frac{\cos\theta - \sqrt{\mu^2 - \sin^2\theta}}{\cos\theta + \sqrt{\mu^2 - \sin^2\theta}} e^{-in\left\{t + \frac{(x\cos\theta - y\sin\theta)}{c}\right\}} \frac{dn}{n^2 - \left(\frac{2\pi}{\tau}\right)^2}.$$

This integral has the same poles and branch cuts as (3) and we could in the same way deduce the expression for the forced vibration. As the operation does not differ from that in the early part of the paper and the result is so well known we may easily omit it. Our interest here centers, as it did in the preceding discussions, on the behavior of the wave immediately after its arrival. We shall proceed therefore as before to a development of the integrand as a power series. The same change of variable is advantageous here and we may set

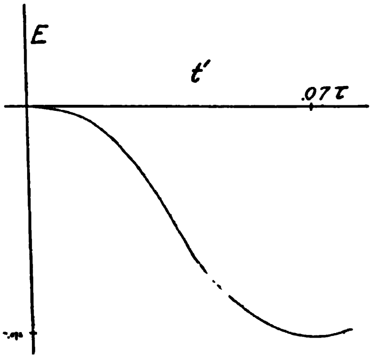

Fig. 2.

$$t' = t + \frac{x\cos\theta - y\sin\theta}{c}.$$

We have already obtained a development of $\sqrt{\mu^2 - \sin^2\theta}$. Substituting we obtain

$$\frac{1}{\tau}\int \left\{ \frac{\varphi_1\beta}{m^4} + \frac{(\varphi_1 + \varphi_2)\beta + \varphi_1^2\beta^2}{m^6} + \cdots \right\} e^{-\frac{2\pi i m t'}{\tau}}\, dm,$$

where

$$\beta = \frac{a^2\tau^2}{16\pi^2 \cos\theta}.$$

Developing the exponential into an ascending series, multiplying into the above and choosing only those terms of power -1 in m which will therefore give residues on integration about the pole $m = 0$, we have

$$-\varphi_1\beta\frac{\left(\frac{2\pi}{\tau}\right)^3}{3!}t'^3 + [(\varphi_1+\varphi_2)\beta + \varphi_1^2\beta^2]\frac{\left(\frac{2\pi}{\tau}\right)^5}{5!}t'^5 - \cdots.$$

This series suggests a sine development with increasing coefficients and first term gone. The order of magnitude of the coefficients is determined by the term containing φ_n with the highest subscript. The order of magnitude of φ_n is that of $(m_0^2)^{n-1}$. $\beta = a^2\tau^2/16\pi^2 = 31$ for $\theta = 0$, a and τ chosen as before. An approximate calculation of the coefficients may easily be made for several terms. The first minimum lines at $2\pi t'/\tau = .45$, $t' = .07\ \tau$. Its ordinate has a value of about .072. The amplitude of the forced vibration in the reflected ray for the same numerical constants, has the value .2. Moreover since t' appears in no lower power than the cube the curve is tangent to the t' axis at the origin (Fig. 2). We see therefore just as we did in the case of refraction that the signal front is of high frequency and greatly robbed of energy. Both facts are naturally closely connected with the phenomenon of setting the resonators in vibration and it is only after they have reached their final states of motion that the refracted ray swings into its final deviated position and both waves acquire their maximum amplitudes.

Summary.

By integrating the Fourier integral in the complex plane, a study has been made of the progress of a light "signal" incident obliquely at the plane boundary of a dispersive medium.

1. The forced vibration of the refracted wave has been deduced with the familiar changes in amplitude, phase and state of polarization.

2. An expression has been found for the refracted "forerunners" reducible to the form given in Sommerfeld's paper for normal incidence and small values of time. The forerunners are found in general not to differ from the type described by Sommerfeld except in magnitude of amplitude and period, both quantities decreasing with increasing obliquity.

3. The direction of the refracted ray is found to be a function of the time, varying from the incident direction at the first instant continuously toward the normal.

4. The reflected ray has also a train of forerunners of extremely small amplitude and period. The curve describing this disturbance is however tangent to the time axis at the origin and rises more slowly than the refracted wave to its first maximum.

In addition, I might point out how remarkably this type of integration adapts itself to such problems. The algebra of complex numbers is already indispensable in modern optics and complex integration will not fall behind it in usefulness.

In conclusion I wish to thank Professor Sommerfeld for his kind assistance and invaluable suggestions throughout the progress of this paper.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON THE VARIATION IN THE SENSITIVITY OF MOVING COIL GALVANOMETERS.[1]

BY PAUL E. KLOPSTEG.

DIFFERENCES in throws on the two sides of the null position of a moving coil galvanometer used ballistically result almost entirely from non-uniformity of the so-called radial field, and from slight displacements of the coil from its position of symmetry with the field. For a given quantity of electricity, discharged in opposite directions, a certain angular position with reference to the "geometric null" may be found for which equal throws are obtained. This position is not fixed for different quantities. The logarithmic decrement usually increases with the amplitude, and the variation is not the same on the two sides of the null position. Consequently the ballistic constant may have a different value for each value of the ballistic throw over the entire scale. In a supposedly high grade instrument differences as high as 20 per cent. in the constant have been found.

In a given deflection or ballistic instrument the best condition for proportionality of deflections and throws with steady and instantaneous currents, respectively, obtains when the axis of the coil is coincident with the axis of symmetry of the magnet. To keep these axes coincident when the coil assumes different angular positions it is necessary that the upper suspension terminals be short—so as to avoid the possibility of bent terminals—and parallel to the fiber, and that the lower suspension be so constructed as to exert no lateral force upon the coil. This last named condition is closely complied with if the torque is made small, and if there is no deformation in the regular turns of the spiral. The adjustment of the position of the coil in the field when once carefully made should be easily reproducible when disturbed. A very convenient method is to provide the galvanometer with an adjustable leveling device such as a spirit level, or a plumb-line with a movable indicator. The level or indicator may be set permanently when the desired adjustment of the coil is accomplished.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 31, 1914.

The bifilar action of a twisted strip upper suspension has been found negligible in its effect upon galvanometer sensitivity. The effect of difference in torques for twisting and untwisting of the lower suspension (1.5-mil strip, 7 turns) has been found comparable with experimental error.

Physical Laboratory,
University of Minnesota.

Preliminary Note on a Mercury Vapor Tube Oscillator.[1]

By B. Liebowitz.

A METHOD for obtaining electrical oscillations of frequencies suitable for radio-telegraphy is described. A mercury vapor tube is provided with two mercury cathodes and an iron or graphite anode. Each cathode is connected through a large inductance and resistance to the negative terminal of a high voltage D.C. generator, and the anode, likewise through an inductance, to the positive terminal. An oscillatory circuit is connected between the cathodes. By this means oscillatory currents as large as ten amperes (r.m.s. value) at frequencies of the order of half a million have been obtained, but these oscillations were not steady. Very steady oscillations have been obtained at frequencies of about 35,000. This method seems to be specially adapted for high powers. The experiments are being continued.

It is pointed out that in all oscillators supplied with energy from a constant potential source, at least 50 per cent. of the energy must be wasted in the supply circuit.

Columbia University.

A New Method of Obtaining a Hysteresis Loop.[1]

By W. N. Fenninger.

FOR students beginning the study of motors there had been designed an electromagnet to show that the force on a conductor placed in a magnetic field is given by the well-known expression $F = I'H'L'/10$, when the proper units are used. The pole faces of this magnet were accordingly made long and narrow (about 15 cm. by 4 cm.). Between the poles was placed a wire, each end of which dipped into a mercury cup. This wire was suspended by two dial spring balances, which could be raised or lowered easily so as to keep the wire always at the same height. It occurred to the author that this apparatus could be used to obtain a hysteresis loop. Since N, the number of turns on the coils of the electromagnet, and L, the length of the coils, were known, the magnetizing force can be computed from the usual expression $H = 4\pi NI/10L$. If we take the expression given above for the

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 31, 1914.

force on a conductor, and solve it for H', the intensity of the field, we get $H' = 10F/I'L'$. A current of 100 amperes in the conductor gave a maximum pull of a little more than 20 ounces on each balance. Tenths of an ounce were read on the balances. The current in the field was varied by small steps so as to have the iron pass through the hysteresis cycle, and a hysteresis loop was plotted from the results. The points fell on a smooth, closed curve, excepting two which deviated less than one per cent. The points in favor of this method are that there is no need of demagnetization to obtain the loop, that each determination of the flux is independent of every other determination and that the deflections to be read are steady ones and not momentary throws. One special advantage is the facility with which the closing of the loop may be checked. Aside from the simplicity of mechanical manipulation, the method has certain pedagogical advantages.

PRATT INSTITUTE, BROOKLYN,
Dec., 1914.

VAPORS WITH POSITIVE SPECIFIC HEAT IN ENERGY CONVERSION.[1]

By J. E. SIEBEL.

IN this paper the author finds that the rate of energy conversion in an ideal complete reversible cycle, operated with a saturated vapor possessing a positive specific heat, like ether, is less than the maximal rate of conversion in a similar cycle operated with superheated vapor of ether.

The latter cycle follows the Carnot rate of efficiency while the efficiency of the saturated vapor cycle is expressed by

$$W = \frac{Q(t - t_0)}{T} - \frac{Q_1(t - t_0)}{T},$$

in which formula W represents the work obtained in reversible conversion between the temperatures t and t_0 when Q signifies the initial heat of vaporization at t degrees and Q_1 the heat which must be abstracted in the expansion stage in order to keep the vapor in a saturated condition. T represents the absolute temperature equal to "t" degrees common temperature.

The above formula as will be seen is a perfect analogon to the formula given in a former paper (abstracted in PHYSICAL REVIEW, April, 1914) for energy conversion with saturated vapors having a negative specific heat like steam, the only difference being that the + sign in the right hand side of the equation is replaced by a — (minus) sign in the equation applying to vapors with positive specific heat.

This difference is explained by the fact that in the former case heat is added by condensation of part of the vapor, while in the latter case heat is abstracted by evaporation of liquid introduced in the expansion stage in addition to the vapor.

CHICAGO, January, 1915.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 31, 1914.

Second Series. *April, 1915* *Vol. V., No. 4.*

THE

PHYSICAL REVIEW.

THE MECHANICAL EQUIVALENT OF LIGHT.

By Herbert E. Ives, W. W. Coblentz and E. F. Kingsbury.

1. Introduction.
   - Previous determinations.
   - Their deficiencies, due to imperfect ideas of light-power radiations.
2. Definition of Light and Luminous Quantities.
   - Light relationships on the basis of definite light evaluating factors.
3. Methods for Determining the Mechanical Equivalent.
   - All involve measurement of the same luminous flux in both watts and lumens. This derivable from:
     1. Value of radiation as radiant power.
     2. Value of radiation as luminous flux.
     3. Luminous efficiency of radiation.
   - Method *A*. Graphical method, from known distribution of energy through the spectrum.
     - *B*. Mechanical evaluation of power as light, by the use of absorbing media or equivalent means.
     - *C*. The measurement of a selected monochromatic radiation.
4. Apparatus and Methods of the Present Investigation.
   - (*a*) Apparatus for method *B*.
     - Luminosity curve solution. Discussion of various luminosity curves available.
   - (*b*) Apparatus for method *C*.
     - Description of apparatus. The measurement of the monochromatic radiation as light.
   - (*c*) The measurement of radiant power in absolute units.
     - The thermopile and auxiliary galvanometer.
     - The radiation standard.
5. The Measurements.
6. Discussion of the Results.
   - The luminous equivalent of the green mercury radiation.
   - The agreement between the two methods and its significance.
   - The weight to be given to the two methods.
   - Various checks on the order of the magnitude of the results.
   - The reproducible character of the measurements given.
7. Summary.

INTRODUCTION.

THE mechanical equivalent of light has been the subject of investigation by Tumlirz,[1] Angstrom[2] and others. Knowing as we do that

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[1] Annalen der Physik, 38, p. 650, 1889.

[2] Annalen der Physik, 67, p. 648, 1899.

objective light and radiant energy are one and the same thing, it is but natural that attempts should be made to obtain the one in terms of the absolute units in which the other is specifiable. These early measurements, with which the term "mechanical equivalent of light" has been associated, were most unfortunately based upon a hazy and immature idea of what constitutes "light." Under this condemnation must fall as well numerous determinations of "luminous efficiency," for the two quantities are of necessity closely interrelated. In brief, light has been considered merely as radiation that can be seen, quite irrespective of the widely different capacities of the various "visible" radiations to excite the subjective sensation of light. As a consequence the physically determined "luminous efficiencies" and "mechanical equivalents" (this latter different for every light source) have no definite relationship to the "efficiencies" and "specific consumptions" used by the engineer. These latter are rational and consistent quantities (which the physical ones are not), though unfortunately related to the chance dimensions of the first measured candle instead of to the C.G.S. units. The present investigation was undertaken to establish on a consistent scheme, in terms of the fundamental physical units, the real values of the light units now in practical use.

The relationship between light and power upon which this work is based are developed in a paper by one of the present writers under the title: "The Primary Standard of Light,"[1] to which reference may be made by those unfamiliar with the subject. In that paper it is proposed that light be defined as radiant energy flux evaluated according to its capacity to produce the sensation of light. It is further proposed that the standard of luminous flux be one watt of radiation of maximum luminous efficiency. More mature thought on the subject suggests, however, that this statement of the proposed standard is more complicated than need be. Accepting the definition of light there given, it is quite sufficient to say that *the unit of luminous flux shall be the watt.* The determination of the mechanical equivalent of light, therefore, becomes merely the fixing of the lumen in terms of the watt.

2. DEFINITIONS OF LIGHT AND LUMINOUS QUANTITIES.

The discussion of this subject can be much shortened by adopting at the start a set of definitions of the quantities frequently entering in. These are taken partly from those now in technical use, and partly either taken or adapted from a list suggested by Ives.[2]

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[1] Ives, Astrophysical Journal, XXXVI., No. 4, Nov., 1912, p. 322.

[2] Lighting Journal, Vol. 1, Oct., 1913, p. 250.

Power consumed by a light source = P; expressed in watts, a portion of which is dissipated by radiation, the remainder by conduction and convection.

Power radiated by a source = $R = \int_0^\infty R_\lambda d\lambda$ = power emitted by a light source in the form of radiation between wave-lengths 0 and ∞, expressed in watts.

Radiation efficiency = R/P = ratio of the power dissipated as radiation to the total amount of power consumed by the source (a pure numeric).

Luminous flux = F = radiant power evaluated according to its capacity to produce the sensation of light.

Light evaluating factor or stimulus coefficient of any radiation is the ratio of the luminous flux, in its appropriate units, to the radiant power producing it, in its appropriate units.

The luminous efficiency of any radiation = L_R, = the relative capacity of the radiation to produce the sensation of light, compared with the capacity of the same quantity of radiation of the maximum possible light producing capacity (a pure numeric).

The total luminous efficiency of a light source = L_r = the relative capacity of the power applied to a light source to produce the sensation of light, compared with the capacity of the same quantity of power in the form of radiation of maximum possible luminous efficiency (a pure numeric).

Units.—Luminous flux is connected to radiant power by a numerical evaluating factor. The unit of power is the watt. The present arbitrary practical unit of luminous flux is the lumen. The light evaluating factor or stimulus coefficient is consequently expressed in lumens per watt. If for this evaluating factor is taken the *luminous efficiency* as above defined, the unit of luminous flux is the same as that of radiant power or applied power, namely the *watt.*

In order to go over to the watt as the unit of luminous flux it is necessary to know the:

Mechanical Equivalent of Light = the value of the lumen in watts of luminous flux.

The simplicity of these relationships is illustrated by the equation,

$$\text{Power consumed} \times \text{radiation efficiency} \times \text{radiant luminous efficiency} = \text{luminous flux},$$

in which every quantity of interest in the study of an illuminant finds its place.

This simplification is only possible if there does exist a definite practically establishable "radiant luminous efficiency." Put another way this means that there must exist a definite luminosity curve of the spectrum. While this latter is actually a function of intensity, size of the field of view, etc., reasons have been given elsewhere[1] for believing that the practical situation is adequately met by the adoption of a high intensity luminosity curve as determined by a certain set of photometric conditions. For this will be used the luminosity curve of the normal equal energy spectrum as determined by Ives as the mean of 18 observers and the same curve as determined by Nutting[2] as the mean of 21 observers. As will be seen, the present investigation offers a means of deciding between these slightly different curves.

3. METHODS FOR DETERMINING THE MECHANICAL EQUIVALENT.

In general the determination of the mechanical equivalent of light consists in the measurement of the same luminous flux in both watts and lumens, from which measurement the ratio of the two can at once be determined.

It usually happens, however, that the radiation is not presented to the energy measuring instrument already evaluated as "light," consequently this value must be deduced from the value of the total radiation and its radiant luminous efficiency. It may happen too that the value of the radiation must be deduced from the total input through a known or probable value of the radiation efficiency. According as one or other of these contingencies is met we find three fairly distinct experimental methods of approaching the problem, as follows:

A. Through the graphical evaluation as light of a known energy distribution.

This may be illustrated by calculations on a black body. Thus Nernst[3] has measured the brightness of a black body (solid angular luminous flux density per unit area); the radiation constant (solid angular radiation flux density per unit area) has been the subject of numerous measurements,[4] and the distribution of energy through the spectrum may be calculated from the Wien-Planck equation. Now, by multiplying the latter by the radiant luminous efficiency or luminosity curve of the spectrum, of maximum value unity, a "reduced" area is obtained, the ratio of which to the total area is the radiant luminous efficiency. We then have

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[1] Ives, "Studies in the Photometry of Lights of Different Colors," Phil. Mag., July, Sept., Nov., Dec., 1912.

[2] Trans. Illuminating Eng. Soc., Vol. IX., No. 7, p. 633, 1914.

[3] Physikal. Zeit., Vol. 7, p. 380, 1906.

[4] See Coblentz, Bureau of Standards Bulletin, 11, p. 87, 1914.

radiated power × radiant luminous efficiency =
luminous flux in ergs per second or in watts, and (from the candle power measurements) *luminous flux in lumens*,

from which the ratio of the lumen to the watt may be obtained.

A similar case is that presented by the incandescent electric lamp, in which we know the power input, the efficiency losses (approximately), the luminous output in lumens, and the radiant luminous efficiency from energy distribution curves and the luminosity curve of the eye.

Values calculated by this method have been published by Ives and others.[1] Reducing them to what they would be if the luminosity curves here adopted were used, the lumen is found to be about 1/800th of the watt. The defect of this method is that the luminous portion of the spectrum, upon which the evaluating process must be carried out, is an excessively small part of the whole, in which experimental errors of determination or deficiencies in the theoretical formula for energy distribution figure disproportionately.

B. Through mechanical evaluation of a given radiant energy flux as light, by the use of absorbing media or equivalent means.

This method does mechanically what the previous method does indirectly by calculation. Imagine an absorbing screen whose transmission is exactly according to the normal equal energy spectrum luminosity curve of the eye, with a maximum transmission of unity. Measure in absolute units the radiation transmitted through it. Measure also the luminous flux from the same light source in lumens. The figures obtained give the ratio desired.

This method is quite the simplest and most direct, once the spectrum luminosity curve is established and the ideal absorbing medium is at hand. It is the method suggested by Houstoun.[2] Another variation of the same idea is the suggestion of Strache,[3] to form a spectrum, pass it through an opening cut to the shape of the visual luminosity curve, and then measure the radiation in absolute units. No determinations made by this method have been published.

C. The measurement of a selected monochromatic radiation, of known luminious efficiency, as light and power.

This method, which in principle differs in no way from the others, has some advantages. For instance the value obtained for the luminous equivalent of the monochromatic radiation has an independent value in that it can be used with any luminosity curve, not only with the one selected by the experimenter. If the monochromatic radiation is

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[1] Electrical World, June 15, 1911, p. 1565.

[2] Proc. Royal Soc., A, 85, 275, 1911.

[3] Proc. American Gas Institute, 2, 401, 1911.

selected near the maximum of visual sensibility the resultant value is largely independent of errors in the determination of the ends of the luminosity curve, since the maximum is fairly well agreed upon.

The great difficulty in the determination by this method is the measurement of the colored light, for which special methods are necessary. By the other methods the colored-light photometry is performed entirely in the determination of the luminosity curve, since the light source measured can always be of the color of the standard.

All the published experimental determinations have been made by this last method. Drysdale,[1] using the spectrally resolved light of the carbon arc, obtained for yellow-green light 210 lumens per watt. Nutting,[2] by a similar procedure obtained 170 lumens per watt for wavelength .566 μ. Buisson and Fabry,[3] measuring the monochromatic green mercury radiation found the value 690. The first two values are unquestionably much too low, probably due on the one hand to scattered radiation, and on the other to the crudity of the methods of measuring the intensity of the colored light. Fabry's value is of the order of magnitude of the calculated figure, but was confessedly weak on the photometric end. The green light was evaluated by simple direct comparison, several observers being used. Their energy standard was probably in error to some extent (see reference 9), but their value is nevertheless remarkably close to the one here obtained.

4. APPARATUS AND METHODS OF THE PRESENT INVESTIGATION.

The aim in the present work has been: first, to develop methods of attack in which the highest attainable accuracy, both photometric and radiometric, may be obtained, and, second, to establish the value of the lumen in terms of the watt with a degree of accuracy sufficient to make that ratio of immediate use in the technology of light production and utilization.

Both experimental methods above outlined (*B* and *C*) were used. A description of the apparatus and method of use follows:

(*a*) *Method B.*—The most important factor in method *B* is the absorbing medium whose transmission shall be the luminosity curve of the normal energy spectrum. The ideal screen would be one whose maximum of transmission was unity and which absolutely matched the curve in question. But neither of these conditions is absolutely necessary. Any other maximum transmission than unity merely involves the correc-

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[1] Proc. Royal Soc., 80, 19, 1907.

[2] Electrical World, June 26, 1908.

[3] Compt. Rend., 153, 254, 1911.

tion of the value found for the transmitted energy to what it would be were the value unity. If the transmission is not exactly in accordance with the ideal curve it is possible by graphical calculation to determine with considerable accuracy the correction factor to be applied. For this it is only necessary to know the *shape* of the energy distribution in the visible region, not its value relative to the rest of the emission spectrum as in the case of method *A*.

The screen used in this investigation was a solution of certain inorganic salts contained in a parallel-walled glass tank one centimeter in thickness. The composition of this solution is:

Cupric chloride	60.0 g.
Potassium chromate	1.7 g.
Cobalt ammonium sulphate	7.5 g.
Nitric acid, sp. gr. 1.05	15.0 c.c.
Water to	one liter of solution.

The transmission of this solution through the spectrum was measured against that of clear water by means of the sunlight spectro-radiometer described elsewhere.[1] The two tanks were constructed and manipulated as in the previous investigation with photometric absorbing solution described by us.[2] The values obtained are shown in Fig. 1, Curve *a*; in Curve *b* (circles) they are multiplied by the factor 1.3 and compared with the Curve *c*, which is the Ives luminosity curve it is desired to copy. It is evident that the copy of the Ives curve is quite close.

What we are the most interested in is the correction to be applied in the use of this screen under the conditions of the experiment. This is obtained by multiplying the energy distribution curve of the light source employed, at each wave-length by the value of the ideal curve and by the value of the solution transmission. The correction factor is given by the ratio of the areas of the two resulting curves. This process is gone through in Curves *d* and *e*. The energy distribution of the "4-watt" carbon lamp used as light source is taken as being substantially that of a black body at 2,080 degrees absolute, which is calculated from the Wien equation. The ratio of the areas *d* (ideal curve) to *e* (actual curve) is 1.30, which is the factor by which the observed power must be multiplied to obtain the working value, if the Ives curve is used.

The remaining curves of Fig. 1, namely, *f* and *g*, are the luminosity curves as recently determined by Nutting, and the same applied to the "4-watt" lamp. These are included for the reason that the experimental values to be reported upon can be used equally well to determine the mechanical equivalent on the basis of this luminosity curve, which

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[1] Description to be published shortly.

[2] Ives & Kingsbury, Trans. Illuminating Eng. Soc., IX., No. 8, p. 795, 1914.

is slightly different from that of Ives, and can in fact be used to decide between the two, in a manner that will be brought out presently. Nutting's curve, determined in substantially the same way as the older one, differs from it chiefly in approaching its maximum more steeply on each side, by reason of which its area is less. In the case of the "4-watt" lamp this difference of area amounts to eight per cent., so that the correction factor becomes .92 × 1.30 = 1.1975. This difference is perhaps due to the characteristics of the two groups of observers, although it has more the appearance of being due to some instrumental difference. Nutting measured the energy distribution of his source at the slit of his observing telescope directly, while Ives had to get his indirectly. While the direct procedure is preferable it may be rendered less accurate by the presence of scattered radiation, apt to be particularly dangerous in the visible spectrum with its small share of the total energy. The Nutting curve agrees, in its shape near the maximum, with the curve determined by Thürmel[1] and others with the Lummer-Pringsheim spectral flicker photometer. As will be shown the agreement or disagreement of methods B and C furnishes a clue as to which curve is the more likely.

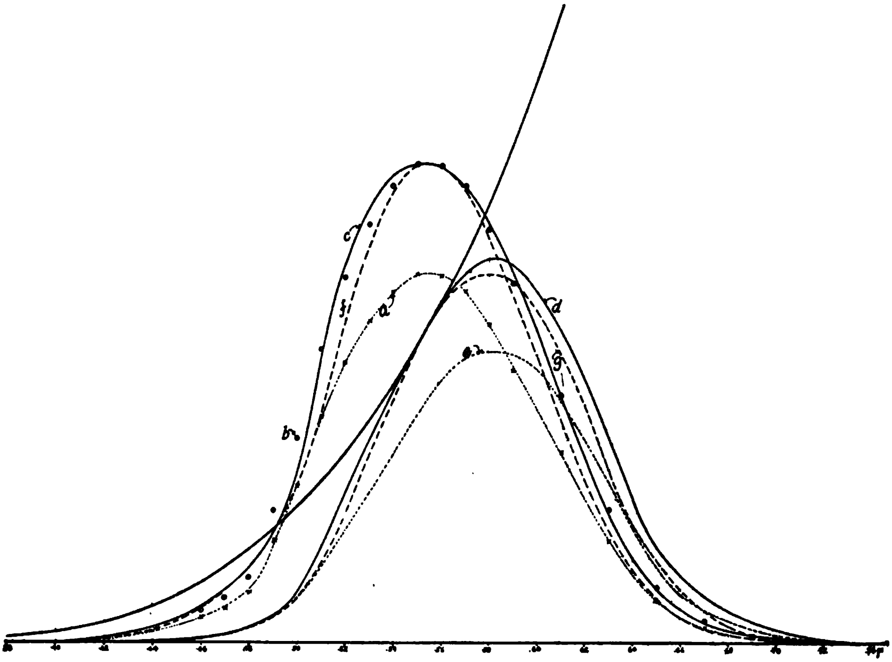

Fig. 1.

Graphical Evaluation of Luminous Flux from "4-watt" Lamp.

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[1] Annalen der Physik, XXXIII., p. 1154, 1910.

The apparatus used for method *B* was a portion of the much more complicated arrangement necessary for method *C*, which is shown in Fig. 2. *G* is the surface thermopile, to be described below, turned to face the radiation standard *R* and the light source *P*. The latter was a "point source" 100 candle-power carbon lamp, set to standard "4-watt" color by comparison with a specially furnished standard from the Bureau of Standards. This was carefully measured for candle-power, through a tank of clear water, in terms of two master standards, also from the Bureau of Standards. Since the transmission of the luminosity curve solution was also measured in terms of clear water, the final result is entirely independent of any possible peculiarities of our pair of matched tanks. The luminosity curve solution is shown in position at *O*. At *N* is a shutter, operated from the observing telescope *F*. *Q* is a sector disc, used to reduce the intensity of radiation from the radiation standard, in order to keep all the galvanometer deflections of the same order of magnitude.

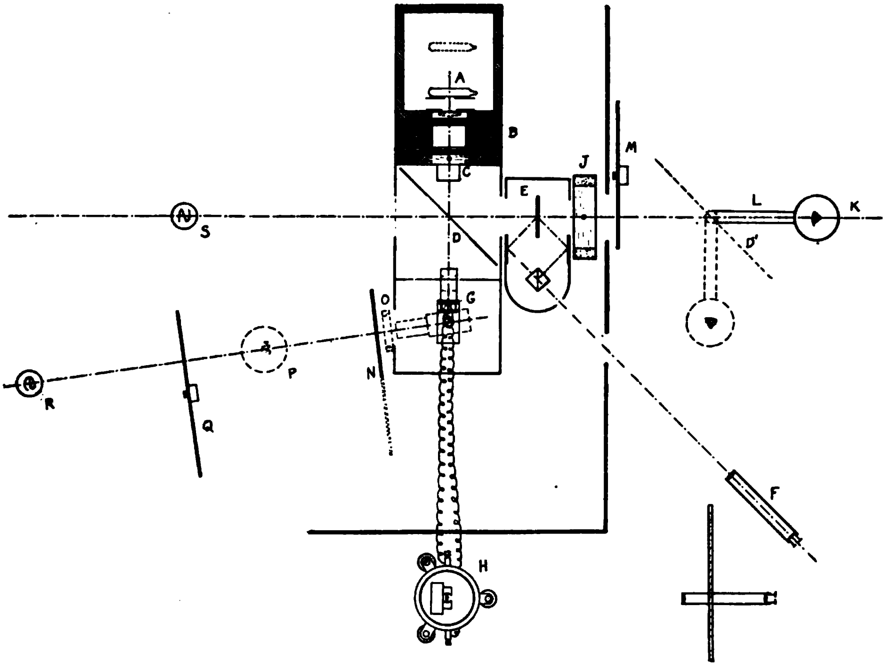

Fig. 2.

Arrangement of Apparatus.

The procedure is first to obtain the sensibility of the thermopile by a set of readings on the radiation standard (the lamp *P* and the solution *O* being of course removed): then with lamp and solution in place, to measure the luminous flux. The candle-power of the lamp, divided by the square of the equivalent air distance (allowing for the absorption of the thermopile window if used), gives the lumens per unit area. The watts per unit area are obtained from the thermopile reading corrected by the ratio already obtained from the measurement of the solution transmission. The ratio of the lumen to the watt can then be immediately derived.

(*b*) *Method C*.—The apparatus for this method is substantially that outlined by Ives in his original suggestion for the watt as the unit of luminous flux.[1] The principal improvement is in the means employed to obtain the photometric value of the green light, which is now made a separate determination, by taking advantage of the researches on colored light photometry and photometric absorbing solutions carried out since the original suggestion was made.

In Fig. 2, *A* is a quartz mercury arc (Heræus 110 volt), *B* is a shutter, operated from a distance, consisting of two parallel sheets of heavy brass, separated by a block of wood, and pierced with round holes with beveled edges. The two elements of the shutter move up and down "straddling" a heavy block of wood having a central opening in line with the axis of the apparatus. At *C* is a glass-walled cell containing a solution of cupric chloride, potassium dichromate and neodymium-ammonium-nitrate, with a little nitric acid. This solution, which was made up empirically, transmits nothing from the mercury arc except the green line .5461 μ, as shown by spectrophotographic and spectroradiometric tests.

At *D* is a transparent mirror of clear white glass. Its function is to reflect a small fraction of the radiation to the Lummer-Brodhun photometer head *E*, while the greater part of the radiation falls directly on the thermopile *G*, which latter is connected with the galvanometer *H*. The thermopile is mounted so that it can be rotated about a vertical axis, the mount being adjustable as to its position in the horizontal plane, while the thermopile can be raised or lowered. By means of these adjustments the pile can be set exactly in the axis of the system and at any desired distance from the arc. The method of performing these adjustments is given shortly.

When the thermopile is turned to one adjustable stop it faces the mercury arc, when turned to the other it faces the radiation standard *R*, which is set accurately at a distance of two meters from the opening of the thermopile, and the shutter *N*, operated from *F*. At *S* is an incandescent lamp candle-power standard. At *K* is a "point source" carbon lamp of the type previously described. *M* and *Q* are sector discs to be

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[1] Energy Standards of Luminous Efficiency, Trans. Illum. Eng. Soc., April, 1911, p. 258.

used when desired. The photometer field is read by means of the telescope *F* which is at such a distance from the thermopile that the body of the observer never comes near it. The whole apparatus is most elaborately protected by a large system of metal and cardboard screens not shown in the schematic figure. By these screens all stray light and radiation are completely excluded.

The various incandescent lamp, standard and comparison, are held constant by voltage readings, on a carefully checked laboratory standard voltmeter connected with the lamps by separate voltage leads carried directly to the sockets. The controlling resistances are all at some distance, so that the heat liberated by them shall have the minimum effect on the thermopile. The mercury arc is connected with an ammeter, but as was anticipated when the transparent mirror scheme was adopted for securing simultaneous photo and radiometric observations, the green radiation cannot be held constant within a hundred per cent. by holding a constant current. Immediately after turning on, the green radiation is only a small fraction of what it becomes after several hours' operation, the current being the same.

From the photometric side the most important part of the apparatus is the glass cell *J*. This is one of a pair, one containing clear water, the other a green solution which transforms the light from lamp *K* to an exact subjective match with the monochromatic green mercury radiation. The composition and the experimental determination of the transmission of this solution have already been described in this journal. It is, therefore, sufficient here to state that by its use the actual photometry of the green light is performed in this present experiment by comparison of lights of the same color, while the evaluation of the green light in lumens is given in terms of the mean value obtained by the 61 observers who measured the solution by the photometric method recommended in the previous investigations quoted.[1] It is not believed that the use of more than 61 observers, taken at random, would have altered the value obtained by one per cent.

Essential parts of the apparatus are the means for putting all parts in optical alignment and for determining the various constants. The mercury arc is furnished with a diaphragm about two centimeters wide, which is considerably smaller than the rest of the diaphragming system at *B* and *C*. In the center of this diaphragm horizontally is a wire cut off so that its point is in the vertical center. In adjusting the position of the thermopile the mercury arc is moved back to the position shown dotted; a lens, also shown dotted, is inserted, which throws an image of

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[1] Ives, Astrophysical Journal, XXXVI., No. 4, Nov., 1912, p. 322; "Studies in the Photometry of Light of Different Colors," Phil. Mag., July, Sept., Nov., Dec., 1912.

the wire point on the photometer screen and on the thermopile mount (or preferably on a ground glass-screen placed in the thermopile mount). The thermopile and photometer head are in the same optical line when this image falls on the center of each. The lens is then removed and the mercury arc so placed that it is seen exactly in the line of the sighting crosslines provided in the photometer head. The thermopile mount is supplied with sighting crosshairs as well, and by their aid the thermopile is properly pointed. When these two adjustments are made the pile is correctly placed except for distance. To set it at the same distance as the photometer screen from the arc, recourse is made to a parallax adjustment. The eye is placed at *S*, where the diaphragm over the thermopile and the photometer screen (half drawn out to furnish an edge) are seen superposed. On moving the eye up and down, the two objects separate unless they are in the same plane. This adjustment, provided the mirror *D* is plane parallel, is quite delicate.

The details of these adjustments have been given at some length because the accuracy of the result is directly dependent on their perfection. In some of the preliminary work attempts were made to increase the amount of energy available by concentrating the mercury light with a lens. It was found that it was almost impossible to line up the apparatus twice alike, as shown by the different values obtained for the ratio of illumination to galvanometer deflection. These troubles entirely disappeared with the apparatus as now described.

Before describing the measurement of the various instrument constants it is advisable to describe the procedure in making a measurement. This may be divided into three parts, as follows:

1. The determination of the sensibility of the thermopile.

This is done by turning the thermopile to face the radiation standard, whose radiation is cut down to some convenient value by the disc *Q*.

2. The simultaneous measurement of the green radiation with the photometer and the thermopile.

This is done with the thermopile turned to face the arc, and with the green solution *J* in place. When the shutter *B* is opened one observer notes the galvanometer deflection, the other moves the comparison lamp *K* until, looking through the telescope *F*, a photometric match is made. The position of *K* and the corresponding galvanometer deflection are recorded.

3. The evaluation of the comparison lamp.

This is done by replacing the solution *J* by the clear water, turning on the candle-power standard *S*, placed at some convenient point, and making a photometric setting by the movement of *K*, the light from which is cut down by the sector disc M. In making this measurement there is again no color difference, and as well, the substitution method is used, eliminating the necessity for reversing the photometer head.

The complete formula used to reduce these observations is as follows:

$$\text{Lumens per watt} = \left(\frac{1}{\mu}\right)\left(\frac{T_R}{R_R}\right)\left(\frac{P_S T_R' T_S T_{TL}}{S_B}\right)\left(\frac{D_{C_1}}{D_S}\right)^2\left(\frac{\theta}{D_C^2 \times \Delta \times W}\right),$$

where

μ = luminous efficiency of the green radiation.

T_R = transmission of reflector D for green light.

R_R = reflecting power of reflector D for green light.

P_S = candle-power of standard S.

T_R' = transmission of reflector D for "white" light.

T_S = transmission of green solution J.

T_{TL} = transmission of glass thermopile window for green light.

D_{C_1} = air distance at which the comparison lamp K gives the same illumination through the clear water tank as the standard lamp S does through the reflector D when placed at the distance D.

θ = temperature coefficient of transmission of green solution J.

S_B = transmission of sector disc M.

D_C = air distance at which comparison lamp K is set when a photometric match is made through the green solution.

Δ = galvanometer deflection, when thermopile is exposed to green radiation.

W = watts per square meter per centimeter deflection.

The last quantity (W) is obtained from the formula:

$$w = \frac{R \times S_A \times T_{TR}}{\delta},$$

where

R = watts per square meter received from the raditaion standard.

T_{TR} = transmission of thermopile window to radiation from standard.

S_A = transmission of sector disc Q.

δ = deflection of galvanometer when thermopile is exposed to standard.

The measurement of these various constants formed one of the most exacting parts of the investigation. The only measurements of unusual character were those on the reflector D. In order to measure its reflection and transmission, arrangements were made by which it could be moved to the position D', and the lamp K was so mounted that it could be turned about an axis in line with the center of the mirror, as shown by the dotted lines. Needless to say, the greatest care was taken to thoroughly clean the reflector and maintain it clean during both its measurement and its use. The measurements of transmission, reflection, etc., were all made several times, since the accuracy of the result is directly dependent upon the accuracy of these.

The values of the constants as determined and used, are as follows: $\mu = .995$ (value from Ives luminosity curve); $\mu = .985$ (value from Nutting luminosity curve); $T_R/R_R = 1/.1083$; $P_S = 10.0$; $T_R = .895$; $T_S = .0437$; $S_A = .2098$; $S_B = .05285$; $T_{TL} = .91$; $T_{TR} = .777$; $R = .88$ watt per square meter.

Using these values the working formula becomes:

$$\text{Lumens per watt} = \frac{62.2}{\mu} \times \left(\frac{D_{C_1}}{D_S}\right)^2 \times \left(\frac{\theta}{D_C^2 \times \Delta \times w}\right).$$

(*c*) *The Measurement of Radiant Power in Absolute Units.* The Thermopile and Auxiliary Galvanometer.—The thermopile used in making the radiometric measurements was of the surface type, having an area of 12 to 17 sq. mm. This area was somewhat reduced by a diaphragm placed in front of the receivers on the glass window which was used in the actual measurements. This diaphragm was of such size that its aperture was always completely filled by the thermojunction surface. The various distances were measured to it, instead of to the receiving surface four or five millimeters behind, which would have been difficult to locate in the parallax distance adjustment. The thermopile consisted of four units joined in series, with a total resistance of about 31.6 ohms.

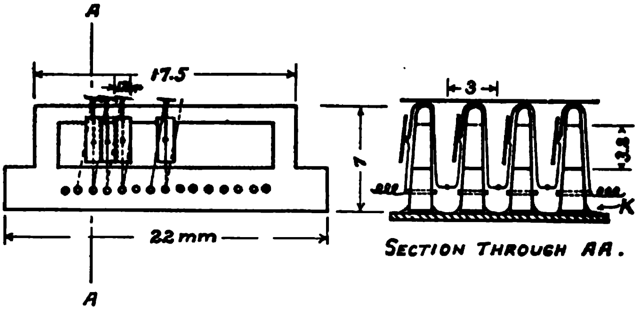

Fig. 3.

Details of Thermopile.

Each unit consisted of 15 thermocouples joined in series as shown in Fig. 3. The receivers were of tin, 1.2 × 3 mm. in area. The thermopile was completely compensated by having receivers upon the unexposed junctions, which were freely suspended in the air, thus admitting a rapid equalization of the temperature, as described elsewhere.[1] By this means drift of the zero reading is reduced to a minimum.

The pile was constructed so that the elements could be joined all (60) in series, or they could be joined one-half (30) in series parallel. When joined all in series the voltage was doubled and the deflections were considerably increased when used with the d'Arsonval galvanometer. When used with a Thomson galvanometer the most efficient combination was the one in which all four units (15 thermocouples in each) were joined in parallel. These incidental details are included here for the completeness of record.[2] The time required to produce a maximum effect upon this thermopile was about 15 seconds, when used with a Thomson galvanometer which had a complete period of about four seconds. This is somewhat longer than usually experienced, and the explanation offered is that the retardation in attaining temperature uniformity in these large receivers is due to the slowness of the heat conduction from the extreme edges.

A glass window was used over the thermopile during the actual measurements for the determination of the mechanical equivalent, thus making the pile practically unsusceptible to drafts of air and to changes of background temperatures and other disturbances likely to be caused by the manipulation of the extensive apparatus used in the investigation. The transmission of this glass for the radiation used to calibrate the radiometer (see below), was determined by a separate measurement under the best conditions.

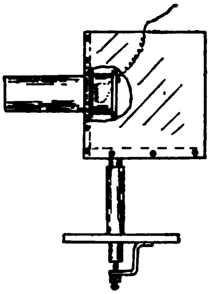

Fig. 4.
Thermopile Mounting

The mounting of the thermopile is shown in the detail sketch, Fig. 4. The protection to radiation and to convection currents is made very complete by the diaphragmed tube *T* and the enclosing box *B*, of bright tin. Still further protection is furnished by a large tin enclosing box indicated in the plan of the apparatus Fig. 2, and by the other portions of the screening system previously mentioned.

The auxiliary galvanometer used was of the d'Arsonval type, and was constructed by Leeds & Northrup. Its sensibility was 33 mm. per microvolt, its internal resistance 13.5 ohms, its external critical damping resistance 32.5 ohms and its period 7.5 seconds.

Although the thermopile resistance was very near the critical damping resistance and the thermopile was quite quick acting, it was found

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[1] Coblentz, Bull. Bureau of Standards, 11, p. 131, 1914, also 9, p. 7, 1912.

[2] See fuller discussion, Bull. Bureau of Standards, 11, p. 131, 1914.

advisable to allow 45 seconds for the deflection to attain its maximum value before reading. This long period is attributable to the fact that the external resistance was not adjusted to meet the requirements for producing critical damping. In a thermopile the voltage attains about 90 per cent. of its maximum value in two seconds; while in tests on the d'Arsonval galvanometer, as ordinarily used, the maximum voltage is applied at once. The damping is no doubt different in the two cases.

In spite of the compensating construction of the thermopile there was a certain amount of slow drift (sometimes amounting to five per cent. of the deflection), due perhaps to the galvanometer. Any uncertainties due to these characteristics of the system were completely eliminated by the experimental procedure, which was as follows:

The thermopile was first exposed continuously for 15 or 20 minutes to radiation of about the value afterwards to be measured. Measurements when started were made on a time basis—the zero was read, a 45-second exposure was made, and then after another 45 seconds, the zero was again read. The zero used was the mean of the two readings. This procedure eliminated the effects of the slight drift except when this changed direction or rate during the reading, such a change, if large, being sufficient cause to discard the reading. (As it happens, during the final readings no drift change occurred which was considered of sufficient magnitude to call for discarding any readings, although the mean variation of the values would probably have been a little smaller had this been done wherever indicated.)

Another precaution taken was to keep all readings of very nearly the same magnitude. This was accomplished by the use of a sector disc over the ratiation standard. All possible errors due to slowness of deflection or variation from strict proportionality between stimulus and deflection (which there is no reason to expect) are avoided in this way.

The precision attained in making the radiometric measurements was very satisfactory, and is illustrated by the representative set of readings below, being the values obtained in the third run by method *C*.

Stimulus = .88 watt per square meter × window transmission (.777) × disc transmission (.2098) = .1432 watt per square meter.

Deflections in centimeters: 3.83, 3.84, 3.82, 3.83, 3.81.

Interval for reading on green radiation,

3.80, 3.76, 3.84,

Interval for reading on green radiation,

3.88, 3.85, 3.83, 3.82, 3.87.

The mean value is 3.83, from which watts per square meter per centimeter deflection = .03745.

The Radiation Standard.—The galvanometer scale was calibrated to give the intensity of the radiation stimulus in absolute value, by exposing the receiver of the thermopile to a standard of radiation, in the form of a seasoned incandescent lamp. This lamp had been standardized for the intensity of the radiant energy in absolute value, at a distance of two meters from the lamp, by direct comparison with the standard of radiation maintained at the Bureau of Standards.[1] This latter, maintained by a set of incandescent lamps, has been established by comparison against a black body, and also by direct measurement, in absolute value, of the energy radiated. The standard of radiation is thought to be accurate to better than 0.5 per cent. The lamp used in the present work was compared with the Bureau of Standards radiation standard before and after the completion of this research, and was found in agreement within one part in 700. The voltage and current calibration was also found in agreement, showing that the characteristics of the lamp had not changed. A further check was afforded by readings on a second radiation standard for which the transmission of the window over the thermopile was not determined. Assuming this to be the same as for the lamp used when both are at the same current, the watts per square meter per centimeter deflection were determined as .0370, to be compared with the mean value obtained from the chief standard (by many readings) of .372. The accuracy attained in the radiation measurements is believed to be quite as high as that in the photometric.

5. The Measurements.

The greater part of the time devoted to the final measurements was spent upon method *C*. This was done partly because of the independent value of the luminous equivalent of the green mercury radiation, partly because the variation in the value of the radiation from the arc with the consequent burden of simultaneous light and power measurements demanded much more attention and care. Three separate determinations were made by this method, between the first and second of which the apparatus was thrown completely out of adjustment and realigned from the start. Two determinations were made by method *B*, one immediately after the first and one after the third by the other method, using the sensibility values determined from them for the radiometer. No more were considered necessary because the possibilities for latitude in the result by this method lie not in the experimental measurements, which are extremely simple, but in the choice of luminosity curve, the measurements of the luminosity curve solution, etc.

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[1] Coblentz, Bull. Bureau of Standards, 11, p. 87, 1914.

The individual readings are recorded in the tables. Under method *C* three sets of calculations are tabulated, namely, the luminous equivalent of one watt of mercury green radiation; the value of a watt of luminous flux in lumens according to the luminous efficiency ascribed to the green radiation from the Ives curve, and the same value when the Nutting curve is used.

These values are:

Lumens per watt of green mercury radiation	613.6
Value of one watt of luminous flux in lumens, Ives curve	616.7
Value of one watt of luminous flux in lumens, Nutting curve	622.2

The three sets of determinations agree to within one per cent.

Under method *B* two sets of calculations are given, one, the watt in terms of the lumen, using the Ives curve, the other, the same quantity as derived from the Nutting curve. The values are:

Value of one watt of luminous flux in lumens, Ives curve	563.6
Value of one watt of luminous flux in lumens, Nutting curve	613.4

The two sets of determinations were in practically perfect agreement.

For reasons given below these figures appear to be decisively in favor of the Nutting curve values. Giving equal weight to the values by the two methods, the value of the mechanical equivalent of light is:

$$1 \text{ lumen} = \frac{1}{617.8} = .00162 \text{ watt of luminous flux.}$$

6. Discussion of Results.

The Luminous Equivalent of the Green Mercury Radiation.—The value to be derived from these observations for the mechanical equivalent of light is dependent on the spectrum luminosity curve which is adopted. The value for the luminous equivalent of the green mercury radiation, on the other hand, is an independent experimental result, depending solely on the method of photometry and the value of the radiation standard. This value—613.6—is thus available for use with any luminosity curve determined by the same photometric method as that used to evaluate the green radiation as light. In view of the fact that all recently determined luminosity curves place the maximum luminosity of the equal energy spectrum close to $.55\,\mu$ and give to wave-length $.5461\,\mu$ an efficiency of at least 98 per cent. it appears safe to say that the mechanical equivalent of light is definitely fixed to within two per cent. by the determination of this constant.

The Agreement Between the Two Methods and Its Significance.—The agreement or disagreement of the two methods is quite independent of the radiation standard employed, and might in fact be studied with any arbitrary working standard. It is dependent upon the self consistency of the photometric method used, upon the accuracy of the luminosity curve and upon the similarity of the visual characteristics of the groups of observers who determined the luminosity curve and the transmission of the monochromatic green solution. If the same group of observers had determined the luminosity curve and the transmission of the green solution then the agreement of the two methods would constitute a test of the accuracy of the luminosity curve and of the ability of the photometric method to add luminosities arithmetically. This latter has been previously established.[2] From our experience in the measurement of the monochromatic green solution we judge it extremely improbable that two groups of 18 observers would differ in their average characteristics as much as the difference exhibited by the two luminosity curves in question. There remains then only the question of the accuracy of the determination of these luminosity curves. That curve must be decided the more accurate which gives the best agreement between the two methods. This means the Nutting curve, by which the two methods agree to one and one half per cent., while with the Ives curve there is an outstanding discrepancy of about eight per cent. This difference between the curves, as already pointed out, is chiefly a difference in their area and may probably be traced back to the indirect means employed to determine the energy distribution in the earlier research.

But while the Nutting curve appears to be more correct, by this criterion, it must not be overlooked that this evidence is not alone sufficient to decide its entire correctness. All that is shown is that the ratio of the luminous efficiencies of the green mercury radiation and the "4-watt" lamp as given by this curve is approximately correct. A whole family of curves could be constructed which would meet this test. For instance, a similar curve with its maximum slightly shifted toward the blue would assign a higher value to the luminous efficiency of the green mercury radiation, which would lower the lumen equivalent of the watt of luminous flux; but this same shift would lower the luminous equivalent of the "4-watt" lamp, with a net result that the two methods would give results in closer agreement. Again, the luminosity curve is not as well determined as the transmission of the monochromatic green solution, as only a third the number of observers were used.

The final value of the mechanical equivalent must wait until all uncertainties in the luminosity curve are removed, but, as remarked above, the value can hardly be in doubt by as much as two per cent. unless some error is present in the green-line determination.

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[2] Ives, "Studies in the Photometry of Lights of Different Colors," Phil. Mag., July, Sept., Nov., Dec., 1912.

The Weight to be Given to the Two Methods.—Having decided on the use of the values derived from the Nutting curve, the question comes up of the relative weight to be given to the two methods. The precision of both sets of measurements is so good that it is believed the outstanding difference is to be ascribed to the uncertainty of the luminosity curve, perhaps to the difference between it and the curve which would be obtained from the 61 observers who measured the green solution. The change called for might affect each value or both. Thus had the measurement of the monochromatic green solution been stopped at 30 observers, the mean would have been 1½ per cent. lower (perfect agreement). Had only the first 21 been taken (Nutting's number of observers) the mean would have been nearly as much lower. It has therefore seemed permissible to give the two values equal weight, remembering that they both lie within the range that would be calculated from the luminous equivalent of the green radiation by any recent luminosity curve.

Method B.

1st Run:

Watts per cm., mean of 11 settings (mean deflection 3.83 cm.).......... .03745

Candle power of "4-watt" carbon lamp.............................44.89

Corrected distance, source to thermopile........................... .479 meters

Corrected deflection = Δ'. Ives, 1.30Δ; Nutting, 1.1975Δ.

$$\text{Lumens per meter}^2 = \frac{44.89 \times .91}{(.479)^2} = 177.5.$$

Watts per meter² = Δ' × .03745.

$$\text{Working formula. Lumens per watt} = \frac{177.5}{\Delta' \times .03745} = \frac{4740}{\Delta'}.$$

No.	Δ	Δ_I'	Δ_N'	Value of Watt in Lumens.	
				Ives.	Nutting.
1*B*	6.52	8.47	7.80	560	608
2*B*	6.42	8.35	7.67	568	618
3*B*	6.62	8.62	7.91	550	600
4*B*	6.51	8.48	7.78	559	609
5*B*	6.45	8.40	7.71	564	614
6*B*	6.38	8.30	7.62	571	622
7*B*	6.47	8.42	7.74	563	612
8*B*	6.45	8.40	7.71	564	614
9*B*	6.45	8.40	7.71	564	614
10*B*	6.39	8.31	7.64	570	620
				563.3	613.3 mean

Various Checks on the Order of the Magnitude of the Results.—A check on the order of magnitude of the result may be obtained by using various data on the efficiency and efficiency losses in incandescent lamps. The greater part of the power input in such lamps is transformed into radiation, and such losses as occur can be fairly closely determined. A loss occurs due to conduction of heat away through the leading-in wires and filament supports. This loss has been measured by Hyde, Cady and Worthing[1] and amounts, in the case of a carbon lamp of the oval anchored filament type, operated at 4.85 w. p. m. s. c. to between four and five per cent. in efficiency. Another loss is caused by the absorption of radiation by the glass bulb. This absorption is much greater for the long-wave heat radiation than for light. The absorbed radiation is in part carried away by convection and conduction. Drysdale[2] found by experiment that this loss amounted to two or three per cent. of the applied power. Another part of the absorbed radiation is re-directed as radiation of much longer wave-length. The distribution of intensity of this radiation around the lamp will be somewhat different from that of the light. It will be more nearly spherical, with a consequent still further loss of power in certain directions, notably the horizontal. This long-wave radiation will also suffer some loss by absorption through the air. There is, therefore, a difference to be expected between the total efficiency of an incandescent lamp of this type and its radiant efficiency of probably not less than seven or eight per cent.

2d Run:

Watts per cm. (13 settings, mean value 3.83 cm.)	.03745
Candle power of "4 watt" lamp	44.89
Corrected distance, lamp to thermopile	.564

$$\text{Lumens per meter}^2 = \frac{44.89}{(.564)^2} \times .91 = 128.0.$$

$$\text{Watts per meter}^2 = \Delta' \times .03745.$$

$$\text{Working formula. Lumens per watt} = \frac{128}{\Delta' \times .03745} = \frac{342}{\Delta'}.$$

No.	Δ	Δ_I'	Δ_N'	Value of Watt in Lumens.	
				Ives.	Nutting.
11*B*	4.63	6.02	5.54	568	617
12*B*	4.59	5.97	5.48	573	624
13*B*	4.67	6.08	5.58	562	612
14*B*	4.71	6.13	5.63	558	608
15*B*	4.65	6.05	5.56	556	614
16*B*	4.67	6.08	5.58	562	612
17*B*	4.70	6.12	5.62	559	608
				564.0	613.6 mean

The radiation standard lamp used is of the type of filament just described. It matches the candle-power standards at 103.5 volts. At this voltage it gives an illumination of 2.785 lumens per square meter at

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[1] Trans. Illum. Eng. Soc., 6, p. 238, 1911.

[2] Proc. Royal Soc., A, 85, 275, 1911.

Method C.

1st Run:

Temperature at beginning, 21°; at end 22.5°, mean = 21.75°.................θ =.989

W, mean of eleven readings in three sets, during and at end of run (mean value of deflection 3.83 cm.).. =.03745

$$\left(\frac{D_{C_1}}{D_s}\right)^2 = \left(\frac{.405}{.798}\right)^2 = .258$$

Working formula, $\dfrac{62.2 \times .258 \times .989}{\mu \times .03745 \times \Delta \times D^2}$, giving, lumens per watt

of green mercury radiation.................................. = m = $\dfrac{424}{\Delta \times D_C^2}$,

ratio of the lumen to the watt of luminous flux, Ives curve..... = M_I = $\dfrac{426}{\Delta \times D_C^2}$,

ratio of the lumen to the watt of luminous flux, Nutting curve = M_N = $\dfrac{430}{\Delta \times D_C^2}$.

	Δ	D_C	$\Delta \times D_C^2$	m	M_I	M_N
1*C*	1.47	.702	.726	584	587	592
2*C*	1.63	.647	.683	621	625	630
3*C*	1.85	.618	.707	600	603	608
4*C*	2.91	.487	.692	613	616	622
5*C*	3.48	.4455	.691	614	617	622
6*C*	3.80	.4275	.695	610	613	619
7*C*	3.93	.421	.697	609	612	617
8*C*	4.04	.418	.707	600	603	608
9*C*	4.04	.4415	.685	619	622	628
10*C*	4.05	.413	.691	614	517	623
11*C*	4.01	.414	.687	617	620	626
12*C*	4.02	.413	.686	619	622	627
13*C*	4.10	.4115	.695	610	613	619
14*C*	3.98	.4185	.697	609	612	617
15*C*	3.92	.4155	.677	626	629	635
16*C*	4.05	.417	.705	602	605	610
17*C*	3.91	.4195	.688	616	619	625
18*C*	3.95	.416	.684	620	623	629
19*C*	3.96	.4165	.687	617	620	626
20*C*	3.98	.4185	.698	607	610	616
				611.4	614.4	619.9 mean

two meters' distance. It also gives .975 watt per square meter at this distance. Hence its radiated lumens per watt = 2.858. The lumens per watt input = 2.597. The efficiency loss is therefore nine per cent. of the order of magnitude indicated by the considerations above. This measurement gives a check merely on the radiation standard. A check on the value for the mechanical equivalent is obtained by a supplementary measurement of luminous efficiency.

The large point-source carbon lamp at "4-watt" color was measured for radiant luminous efficiency by determining the ration of the radiant power to the radiant power transmitted by the luminosity curve solution (the latter being, according to definition, luminous flux).[1]

Correcting for the actual transmission curve of the solution as compared with the Nutting curve, the radiant luminous efficiency was found to be .0045. Now .0045 times 417.7 is 2.78 = radiated lumens per watt. The lumens per watt consumption = 2.59. From this the efficiency loss is seven per cent.—a satisfactory check with the other values. This check is of course practically method *B*, except that the power transmitted by the luminosity curve solution is obtained indirectly by two separate experiments.

2d Run:

Temperature throughout 23°..$\theta = .982$

W, mean of 8 settings in two groups (mean deflection 3.88 cm.)................ $= .0366$

$$\left(\frac{D_{c_1}}{D_s}\right)^2 = \left(\frac{.406}{.798}\right)^2 = .259.$$

Working formulas:

$$m = \frac{432}{\Delta \times D_c^2},$$

$$M_I = \frac{434}{\Delta \times D_c^2},$$

$$M_N = \frac{438.5}{\Delta \times D_c^2}.$$

	Δ	D_c	$\Delta \times D_c^2$	m	M_I	M_N
21*C*	3.43	.456	.714	607	610	614
22*C*	5.41	.360	.702	616	619	625
23*C*	5.88	.342	.688	629	632	637
24*C*	6.03	.338	.690	627	630	635
25*C*	6.12	.340	.708	611	614	619
26*C*	5.99	.346	.717	603	606	611
27*C*	6.06	.3395	.699	619	622	627
28*C*	5.84	.345	.696	622	625	630
29*C*	5.91	.3455	.706	612	615	621
30*C*	5.98	.3465	.719	602	605	609
				614.8	617.8	622.8 mean

The Reproducible Character of the Measurements Given.—A feature of the work here reported, which is believed worthy of emphasis, is that unlike most previous measurements of a similar nature, every element entering into the result may be copied and checked by other observers. The determination is, in short, of a strictly reproducible physical character. This is made possible by recording the factors most difficult to measure in material standards of reproducible or maintainable form.

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[1] A set of determinations of luminous efficiency have recently been made in this manner by Karrer, Physical Review, p. 189, Vol. V., N. S., No. 3, 1915.

Thus the difficult measurement of green light is recorded in the reproducible green solution. The measurement or radiation in absolute value is confided to long-lived incandescent lamps. If in the future either the standard of radiation is changed, or the photometric method here employed is superseded, the ratio of the new to the old value can be applied directly to the value obtained in this investigation without the necessity for repeating the whole piece of work.

The chief uncertainties in the result are on the physiological side, which is here relegated to entirely independent investigations. A general agreement on photometric methods, a definite answer to the question: "What is light?" by the establishment of a representative average eye spectrum luminosity curve—there lies the work of the future. When that is completed the chief uncertainty of the present work can be removed. This uncertainty is however believed to be quite small.

3d Run:

Mean temperature 21.5°...$\theta = .991$

W, mean of 13 settings (mean deflection 3.83 cm.)........................ $= .03745$

$$\left(\frac{D_{c_1}}{D_s}\right)^2 = \left(\frac{.404}{.798}\right)^2 = .256.$$

Working formulas:

$$m = \frac{421}{\Delta \times D_c^2},$$

$$M_I = \frac{423}{\Delta \times D_c^2},$$

$$M_N = \frac{427.5}{\Delta \times D_c^2}.$$

	Δ	D_c	$\Delta \times D_c^2$	m	M_I	M_N
31*C*	3.11	.4675	.680	620	623	629
32*C*	4.14	.405	.680	620	623	629
33*C*	4.68	.380	.677	622	625	632
34*C*	4.75	.381	.690	610	613	619
35*C*	4.76	.3785	.682	618	621	627
36*C*	4.62	.384	.681	619	622	628
37*C*	4.54	.387	.681	619	622	628
38*C*	4.61	.386	.687	614	617	622
39*C*	4.64	.386	.692	609	612	618
40*C*	4.56	.386	.680	620	623	629
				617.1	620.1	626.1
Mean of all observations (*c*).............				613.6	616.7	622.2

7. SUMMARY.

The subject matter of this paper may be summarized as follows:

1. Rational definitions have been given for light quantities. In

accordance with these the mechanical equivalent of light is defined as the value of the lumen in watts.

2. An experimental determination by two different methods gives for the mechanical equivalent of light a mean value of 0.00162 watt per lumen.

The discussion of the significance and importance of this quantity may be brief by reason of the full discussion in the various publications to which reference has been made. Suffice it to say that here luminous flux, on the basis of the accepted definition, can be measured in C.G.S. units, *e. g.*, in watts, and that consequently the watt is a rational standard of luminous flux ("primary standard of light").

The measurement of luminous flux in watts and the establishment of the watt as the standard are dependent on the evaluation of the present standard and units in terms of the watt. The mechanical equivalent of light is therefore the most fundamental quantity in the establishment of light measurement on a physical basis.

Physical Laboratory,
The United Gas Improvement Company,
Philadelphia,
December, 1914.

THE CORONA IN AIR AT CONTINUOUS POTENTIALS AND PRESSURES LOWER THAN ATMOSPHERIC.

BY DONALD MACKENZIE.

SINCE the practical importance of the corona discharge was first realized, the subject has been extensively investigated both in this country and abroad.

The general agreement among observers is that the corona-forming voltage is independent of the material of the discharging conductor and of the humidity of the air; that the critical surface-intensity is greater for smaller wires; that increased temperature or decreased gas pressure decreases the critical voltage; and finally, that the onset of the phenomenon is not affected by the antecedent ionization near the wire.

It was with a view to examine the continuous potential corona at low pressures and so to test the extension of the empirical laws found for the alternating corona that the work here reported was begun. In this laboratory at the present time the only available source of direct current at high potential is a battery of 500-volt, 0.1 kilowatt generators driven by a direct current motor. These generators are separately excited from a lighting circuit, which also furnishes power to the motor; this makes the control of voltage very difficult, the fluctuations in the line voltage amounting at times to three or four per cent. Most of the irregularities of the points plotted for some of the curves are attributable to this condition. The speed control of the motor enables the generated voltage to be raised to more than 900 volts on each machine: at the beginning of the work five such generators were at hand, furnishing a potential of 4,000 volts and more, but two machines broke down before much progress had been made. This limited the total voltage to 2,700 volts, and so placed a regrettable restriction on the dimensions of the corona apparatus and the pressure range.

DESCRIPTION OF APPARATUS.

A diagram of the apparatus used is shown in Fig. 1. *A* is a large glass tube 10 cm. in diameter and 75 cm. long, inside of which is supported by hard rubber rings the brass cylinder *B*, 4.9 cm. in internal diameter and 61 cm. long. These rings are pierced with a number of holes to permit free flow of air through all parts of the apparatus. The glass cylinder is closed at each end by brass plates, cemented on with a mixture of beeswax and rosin. In the center of each of these plates a hole is drilled, permitting the passage of the wire *C*, which is soldered at each end into bushings held by the nuts *DD*. In all cases it was easy to apply sufficient tension to hold the wire straight unless a large current was allowed to pass in the discharge.

The glass tube *A* is provided with three side tubes, two of which serve for the ground connection to the brass cylinder and for the pump connection respectively. The third side tube, the uppermost in the figure, supported another glass tube, sealed into it with sealing wax and drawn down at each end to hold a small brass rod screwing into a brass plate about 2 cm. in diameter. Connection to ground and to the brass rod just mentioned was by small platinum wires sealed directly into the glass tubes. The disk carried on the end of the brass rod *E* is curved parallel to the surface of the brass cylinder, and stands about a millimeter above it. Directly under the disk are a dozen or more small holes in the cylinder, through which charged particles may pass on their way out from the central wire, charging or discharging the electroscope to which the disk is connected.

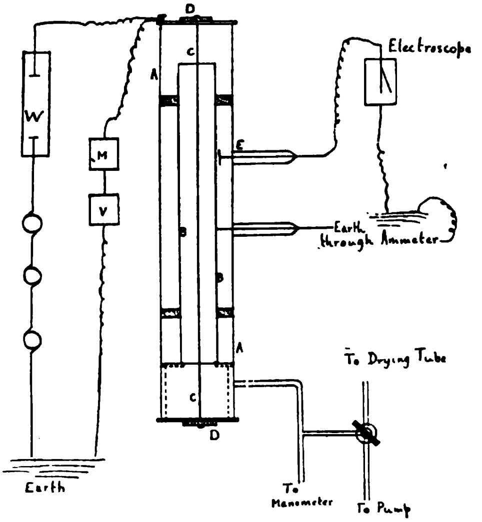

Fig. 1.
Diagram of corona apparatus.

The voltage of the three generators is applied to the apparatus over leads including the water resistance *W*, about 3 cm. in diameter and 75 cm. long, variable by varying the separation of platinum electrodes.

One end of the generators is connected thus to the brass plate closing the glass tube; the other end is earthed, as is the brass cylinder through a milliammeter or galvanometer. Reversal of wire polarity is effected by reversing the excitation of the generators. Measurement of voltage is by means of a Weston D.C. voltmeter V with a multiplier M, reading 150 volts when the wire potential is 3,000.

The apparatus is supported vertically on a table, from which it is insulated by porcelain blocks. To prevent the breaking of the ground connection by slipping of the corona tube, the latter is supported on a hollow wooden cylinder, the walls of which are turned very thin except at the top, where a ring supports the lower end of the brass tube. In immediate contact with the tube is a thin ring of hard rubber; this ring extends into the field no more than a millimeter, and in no case was any irregular behavior of the discharge caused by its presence.

In the upper brass plate are cut holes covered with glass windows. Above these is fixed a mirror permitting visual exploration of the space within the cylinder.

It was expected that a charged electroscope connected with the disk E would be affected by a discharge passing between the wire and the cylinder: a positive corona on the wire should discharge a negatively charged electroscope and vice versa. This expectation was justified: when the corona starts the gold-leaf drops instantaneously and there is no possibility of confusing this effect with a loss of charge due to atmospheric leak. As the voltage is raised, electrostatic induction brings about a partial fall of the gold-leaf: a negatively charged gold-leaf receives an induced positive charge in the presence of the positively charged wire, the corresponding negative charge appearing at the disk E. As long as the potential of the wire is constant the magnitude of the induced charge on the electroscope does not vary, and the definiteness of the observation is not diminished by this action.

The electroscope is charged statically, and the voltage gradually raised until the gold-leaf suddenly falls. The voltmeter is then read and the pressure recorded.

The wires used were carefully straightened by the electric current, except in the case of the larger wires, which were brass rods free from kinks. All were polished with fine emery and crocus cloth, and when put into the tube showed no sign of surface irregularity. Dust particles from the air settling on the wire are of no importance, since unless the wire is sticky they are driven off by electrostatic repulsion. This fact has been overlooked by most observers, who attribute irregular behavior of the corona to dirt which they suppose to have settled on the wire.

The most important step in setting up the apparatus is the centering of the wire in the brass cylinder. The method used is as follows: The end bushings pass through quarter inch holes in the end plates which allow sidewise displacement of the whole wire. When the nuts are tightened to give the tension considered suitable, a scale is placed under the apparatus lying horizontal on the table. The eye is held steady over the scale, which lies just parallel to the end of the brass cylinder. Placing the head at such a distance above the tube that the cylinder subtends at the eye a given number of scale divisions, say 2.5 in., it is possible to judge how far from center is the wire: if the tube covers 2.5 in. on the scale the wire should stand over the 1.25 in. division. If such is not the case, adjustment is made by moving the nut across the end plate, and the apparatus is then turned through 90 degrees to make a second adjustment at right angles to the first. Then the previous adjustment is re-examined and corrected if necessary, and the procedure repeated at the other end. The cylinder of wood at one end of the tube hides the wire, but by gently tapping the end plate opposite, the brass tube can be induced to move away from the wooden ring sufficiently far to permit centering. Then, when both ends are satisfactorily adjusted on the axis of the cylinder, the apparatus is ready for installation. It was found a simple matter to set the wire to 1/200 in.

When the tube has been set in place the air is exhausted by means of a Gaede pump and the space refilled with air drawn through a column of sulphuric acid to exclude moisture. This is repeated a number of times, and the apparatus left exhausted to allow leaks to manifest themselves. With the number of beeswax and rosin seals necessary, leaks could not absolutely be avoided, but they could usually be kept so slight that no alteration in the reading of the manometer could be detected in the time spent in making observations at any one point. When the leakage was faster than this, it was possible to estimate its magnitude and correct the pressures recorded. This occurred in only one case, which will be described later. The pressure was read on a closed mercury manometer connected immediately to the glass tube.

Preliminary Experiments.

The first experiments were made with large wires, 3/32 in. in diameter. The voltage then available was 4,000, and corona formed on such wires at a pressure of about 4 or 5 cm. At once a difference was noted in the positive and negative discharges. With the wire positive, the corona formed at a definite voltage and pressure, disappearing as soon as the voltage was lowered or the pressure raised by the smallest step that could be made. With the wire negative, however, the discharge was of quite different form. At a given impressed voltage, no visible discharge passed until the pressure was lowered well below the value corresponding to the positive corona at the same potential. Finally, however, came on a discharge carrying a large current sufficient to burn out two 16-c.p. incandescent lamps in series in the ground connection. This discharge persisted after the voltage was lowered far below the initial value, and was not extinguished by a moderate increase in pressure. In fact, a discharge setting in, say at 3,500 volts and 4 cm. pressure, persisted up to a pressure of more than 26 cm. Increase in pressure was accompanied by an increase in the current flowing; even at low pressure sufficient heat-energy was liberated to make the glass tube uncomfortably warm.

The water resistance had not been used. It was then inserted in the high potential side in order to keep the current down to a value safe for the generators. On examining the discharge from the negative wire, it was seen to show the characteristic structure of the discharge in high vacua. The appearance will be described presently. Instead of a uniform glow along the whole wire as in the positive effect, the luminosity is confined to a small length of the negative wire.

With the large wires it was possible to obtain the positive corona at the lowest pressures attainable (from 1 to 2 mm.) but the negative corona never appeared: the discharge from the negative wire was always of the vacuum tube type. On removing the wire from the tube it was found deeply oxidized at the points where the vacuum tube discharge had existed.

This singularity is intimately associated with the size of the wire, as will appear from the experiments about to be described.

FINAL RESULTS.

1. *The Positive Effect.*—All of the wires when positive to the tube form coronas at the lowest pressures to which the apparatus was evacuated. The discharge is a perfectly uniform and stable violet or bluish glow extending the whole length of the wire within the brass cylinder. Using the electroscope charged negatively, the gold-leaf is seen to fall sharply at a definite voltage, and keeping the pressure constant this value of voltage may be read any desired number of times. The recorded observations frequently show a disagreement of 20 volts among the readings repeated at a constant pressure: this disagreement is due not to any irregular behavior of the corona, but to the fluctuations in the voltage of the circuit supplying the generators and motor. In the time taken for the observer to note the fall of the gold leaf and thereafter read the voltage,

the voltmeter needle may move in one direction or another and then rest for several seconds. Variations of two or more scale divisions are not uncommon: these mean a variation of 40 to 50 volts in the potential of the wire. When two observers work simultaneously, one noting the electroscope and the other reading the voltmeter, these irregularities do not affect the observation.

It was invariably found for the larger wires that the onset of the visible corona accompanied the discharge of the electroscope. The corona is faint at onset and around small wires can be seen only with well rested eyes; however, it is seen whenever attempted under suitable conditions. Having once verified this expected result I relied thereafter upon the electroscope. With each wire the verification was repeated.

As the voltage is raised above that necessary to start the corona, the luminous sheath expands progressively, accompanied by an increase in the current making the latter readable on the milliammeter. With further increase in voltage a point is reached where the corona is unstable. A slight increase in voltage causes the corona, previously uniform over the whole length of the wire, to collapse to a vacuum tube discharge confined to a few millimeters. The instability of the corona at this transition point is shown by the fact that if the generator excitation and motor speed are kept at the appropriate value and the potential suddenly applied to the wire, corona forms for an instant and then collapses to the vacuum tube discharge. Refilling the tube with cool air and then exhausting anew lengthens the time taken for the change to 4 or 5 seconds. This lag could not definitely be determined owing to the variations in generator voltage. On the establishment of the vacuum tube discharge, the voltage drops 50 or 60 per cent. and simultaneously the current rises to many times its former value.

This form of discharge shows all the structure recognized in the vacuum tube discharge. The negative glow is a thin blue layer against the inner wall of the brass tube, separated from it by a narrow Crookes dark space. The positive column is a pink sheath enveloping (usually, but not always, completely) a centimeter or two of the wire, directly opposite the negative glow which does not go completely around the inner surface of the cylinder but covers an increasing circular extent of it with increasing voltage. Between the positive column and the negative glow is the Faraday dark space; at low currents (total voltage over corona tube and ballast resistance lowered) this space is invaded by the positive column, which becomes striated. Further lowering of the voltage causes the striations to become more distinct, and the positive column extends almost to the point of meeting the negative glow; the latter is greatly diminished in extent and brilliancy. At last, just as the Faraday dark space seems to be completely eliminated, the discharge ceases. The same sequence of phenomena is seen when the pressure is allowed to increase. After cessation of the discharge the voltage between the wire and tube rises to the value appropriate to an inactive field.

Increasing the total voltage increases the current carried; the voltage on the tube and wire slowly decreases. Decreasing total voltage decreases the current at the same time that the tube-wire voltage gradually increases.

2. *The Negative Effect.*—For the larger wires used in my experiments the negative corona is not obtainable: the first detectable discharge is the vacuum tube discharge. For the smaller wires the case is different. At the lowest pressures the vacuum tube discharge is the only one obtainable. At higher pressures the negative corona appears, expands with increase of voltage above the critical value, and gives place to the negative vacuum tube discharge at a transition point determined, as in the positive effect, by the pressure and the wire diameter. After the vacuum tube discharge has been established the current and tube-wire voltage vary as in the positive effect. The cessation of the discharge is after the same sequence of changes in the two cases.

The negative corona is never a uniform sheath like the positive. It is grouped about bright blue points set at intervals along the wire; these blue points are surrounded by reddish streamers, and increase in number as the voltage increases. With decreasing voltage the blue points are the last to disappear: they persist at a voltage lower than that at which they form.[1]

After transition, the structure of the discharge is the same as the positive vacuum-tube discharge, but reversed: next to the wire is the Crookes dark space surrounded by the negative glow, cylindrical in form; then comes the Faraday dark space and after it the positive column flat against the surface of the tube.

The negative glow may appear outside the uniform field, at the very end of the wire—the positive column collecting in a restricted area at the edge of the brass tube. The discharge may start in the interior and climb up more or less rapidly to the end of the wire. This is probably due to convection currents, set up even in rarefied air by the very hot discharge. This explanation is suggested by the fact that if the voltage is suddenly removed and reapplied, the renewed discharge prefers points

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[1] Since these observations were made, experiments by Farwell have shown that the negative corona is invariably that described above, and that the number of the blue points on the wire is characteristic of the voltage. Farwell, PHYS. REV., 4, 2d Series, 31–39, 1914.

which have just previously been discharging. It is reasonable to suppose that the air in this neighborhood is in a favorable condition to initiate the discharge, being adjacent to the most highly heated portion of the wire. Convection currents raise this hot air, making conditions less suitable at the lower end and more so at the upper end of the existing discharge column.

The energy of the discharge is sufficient to heat to redness the wire and partially to oxidize the wall of the tube: after prolonged discharge a green color is seen in the field. In both positive and negative effects at very low pressures (for this apparatus) the Crookes dark space is seen to lie over a negative layer. This luminosity adjacent to the cathode, accompanying the ionization of the gas by the canal rays, is more readily recognized at low pressures because of the greater length of the Crookes dark space.

Description of Observations.

The observations at each point were considered satisfactory if no readings of the voltmeter differed from the mean by more than one half a volt; this variation was unavoidable because of fluctuations. The multiplier ratio being 20 to 1, this means that a disagreement of 10 volts was considered tolerable. The accuracy of the observations may be judged from the following table, showing some of the readings for the negative corona on a nickel wire, diameter 0.063 cm.:

Pressure in mm.	Voltmeter Readings.	Voltage.	Pressure in mm.	Volmeter Readings.	Voltage.
69.8	124.0	2,480	56.5	110.0	2,200
	123.8	2,476		110.0	2,200
	123.0	2,460		110.0	2,200
	124.0	2,480		110.0	2,200
62.5	116.5	2,330	48.2	101.0	2,020
	117.5	2,350		100.0	2,000
	117.0	2,340		100.0	2,000
				101.0	2,020

Wires of diameter 0.165 cm., 0.157 cm., 0.107 cm. and 0.063 cm. were all investigated using the electroscope as a detector of the onset of the corona. For the negative effect when no corona can be formed, visual observations were relied on: the behavior of the electroscope is irregular when the tube is sustaining a vacuum tube discharge unless the region involved lies directly under the disk E: in this event the positively charged electroscope is immediately discharged and then receives a negative charge.

When associated with the smallest wire, 0.042 cm. in diameter, the electroscope gave evidence of an ionization current unaccompanied by luminosity. At pressures even higher than one-half an atmosphere, the charged wire had an influence on the electroscope. Several electroscopes of different form and size were tried, but all behaved in the same way: the electroscope charges spontaneously, the sign of the charge being positive when the wire is positive, negative when the wire is negative. The more sensitive electroscope charged until the gold leaf touched the

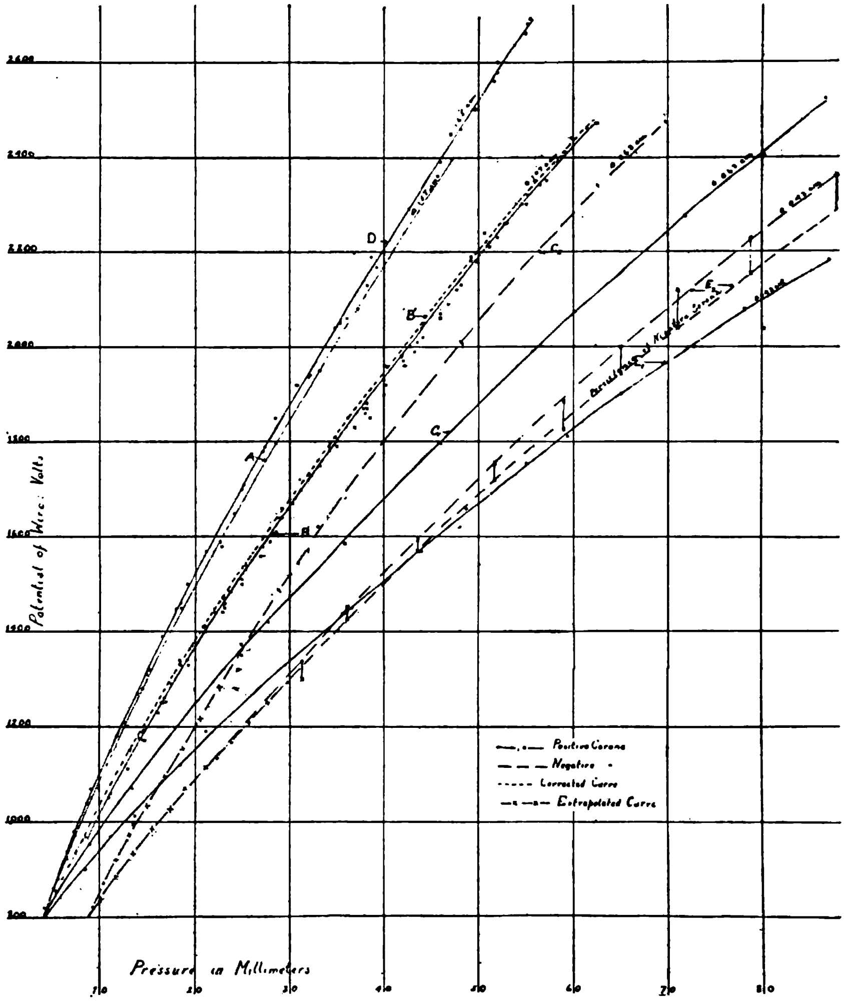

Fig. 2.

Corona-forming voltage. Diameters: A, 0.157 cm. +; B, 0.107 cm. +; B^1 is B corrected or leak; C_1, 0.063 cm. +; C_2, 0.063 cm. − ; D, 0.165 cm. +; E_1, 0.042 cm. +; E_2, 0.042 cm. −.

grounded case inclosing it, after which it fell back and the process repeated itself continuously.

Accordingly, the attempt to detect corona formation by the electroscope was given up for this size of wire, and in place of the milliammeter there was substituted a galvanometer, giving a deflection of one scale division for 7×10^{-6} amperes. The suitability of the galvanometer for this work (at least under these conditions) is shown by a comparison of curves A and E_1, Fig. 2.

Observations with the galvanometer are made as follows: The observer watches the galvanometer, at the same time slowly raising the voltage, and at the first perceptible deflection of the needle he reads the voltmeter. The experiment is repeated until the observer becomes accustomed to noting very small deflections and has convinced himself that they occur at the same value of voltage each time, and are simultaneous with the appearance of the corona. He then proceeds with the same program as when using the electroscope.

Curve B, Fig. 2, is plotted from observations on a steel wire of diameter 0.107 cm. During these observations the leak of air into the apparatus was quite rapid and efforts to overcome it failed. Accordingly it was decided to let the apparatus leak and make observations in the following way: The electroscope was charged, the voltage raised until the gold-leaf fell, then the pressure read immediately and the voltmeter last. As soon as possible the electroscope was re-charged and the series of operations repeated. This gave a new pressure reading, by reason of the leak during the interval between the two observations. Five series of such observations were made and all observations plotted on the sheet. Through them a smooth curve B was drawn, and this curve corrected for leak. The following considerations enabled the correction to be made:

The pressure rises 5 cm. in ten minutes, or 5 mm. per minute. The time taken to note the discharge of the electroscope and read the manometer is approximately six seconds or one tenth minute. In this interval the pressure has risen 0.5 mm.—it is that much higher than it was at the instant the electroscope was discharged. The correction, then, is to shift the plotted curve to the left on the sheet through a distance corresponding to 0.5 mm. in pressure. Curve B', Fig. 2, results.

Special investigation was made to determine the influence of temperature variation on the corona-forming voltage. It was found that within the limits of variation of room temperature during observations (19° to 21° centigrade), such as influence is not appreciable.

COMMENT ON CURVES.

The intersection of the positive corona curves by the negative curves for the same wires is of the greatest interest. It has been suspected for some time that under certain circumstances the positive and negative coronas begin at different voltages. The difference varies with the size of wire and the pressure. In the case of each of the two wires for which observations of the negative corona were possible, there is a pressure below which the positive critical voltage is higher than the negative, while above this pressure the negative starts at the higher voltage.

The intimate relationship of the negative corona to the pressure and the size of wire is well shown in the curves. The 0.063 cm. wire forms a stable negative corona only at pressures above 25 mm. The 0.042 cm. wire gives a stable negative corona as low as 19 mm. This peculiarity of the negative corona has not, it is believed, been heretofore recorded.

The lower curve E_2 of Fig. 2 represents the observation that as the voltage is gradually lowered below that corresponding to the first deflection of the galvanometer needle, the negative corona persists for a time. The interval of voltage during which it continues to be observable on the galvanometer is indicated by the vertical lines.

E. A. Watson[1] has worked with the corona in cylindrical fields. He was able to use continuous potentials up to 70,000 volts, derived from an influence machine of special design. The wires used ranged in diameter from 0.070 cm. to 1.276 cm., and the pressure was varied from atmospheric down to 35 cm. He describes the same difference in the appearance of the two coronas as that observed here and finds that the negative corona starts at a higher voltage than the positive on the same wire. Watson found no region of pressure where the negative corona failed to appear.

V. Schaffers[2] has studied the continuous potential corona at atmospheric pressure, using extraordinarily small wires, 0.0003 cm. to 0.35 cm. He concludes that the ratio of the potentials critical for the positive and negative coronas varies regularly with the radius of the wire: for $r = 0.01$ cm. the two potentials are equal; for r less than this, the negative is lower than the positive; for r greater than 0.01 cm. the positive is the lower. These results refer to atmospheric pressure only, but tend to confirm Watson's observations and those of the present paper.

Investigators of the alternating corona have usually thought that the corona forms on the two half waves at the same value of instantaneous voltage. This conclusion is rendered doubtful by the experiments of

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[1] Electrician, *63*, 828, 1909, and *64*, 707, 1910.

[2] Comptes Rendus, *157*, 203–206, 1913.

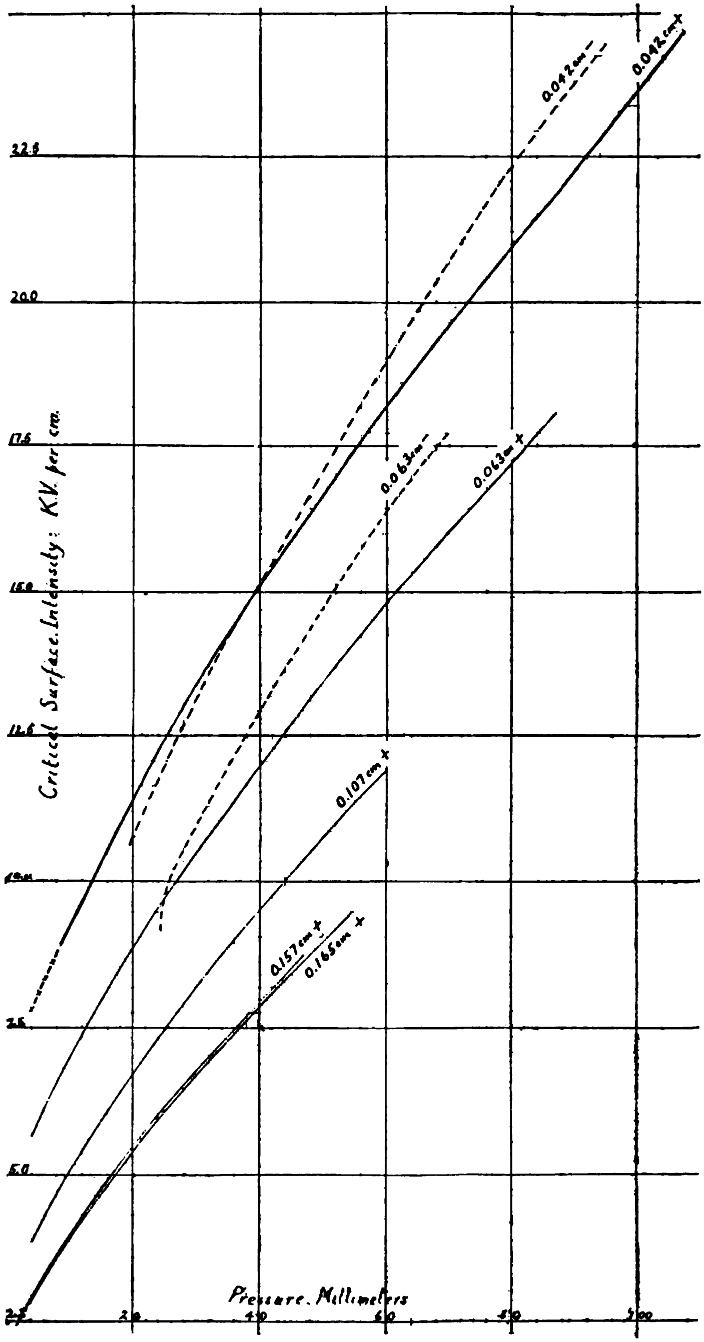

Fig. 3.

Critical surface-intensity. Solid curves indicate positive corona; dotted curves indicate negative corona.

Bennett,[1] who made an oscillographic study of the corona-current and voltage. When no corona discharge is taking place, the current oscillogram records only the charging current of the apparatus,—a pure sine wave. As the voltage is gradually raised to the critical value, the charging current recorded by the oscillograph remains a sine wave until the corona voltage is reached. At this point the charging current is broken by humps: a smooth hump for the positive corona, an oscillatory disturbance for the negative. Also the negative hump is more pronounced. This is in accord with the observations made here when using the galvanometer to detect the corona. It was found that the least perceptible deflection of the needle was a small fraction of a scale division for the positive corona; for the negative, however, the swing is through several scale divisions no matter how carefully the voltage is raised.

If it is true that one corona forms at a lower voltage than the other, then if the pressure and voltage are appropriate the corona tube should rectify the current due to an alternating potential. An experiment to test this was carried out with a 20 : 1 transformer, excited by 110 volts, 60 cycles. The pressure was adjusted to 85 mm. around the wire of 0.042 cm. diameter. This pressure corresponds for this wire to a positive critical potential lower than the negative. On closing the secondary circuit of the transformer and raising the voltage to the critical value, a steady deflection of the galvanometer needle occurs, corresponding to a positive current, *i. e.*, from wire to grounded cylinder. With increase in voltage the deflection is reversed: the negative current is larger than the positive. Thus the corona tube acts as a rectifier, the sign of the rectification depending on the value of the impressed voltage. No facilities were available for making a thorough investigation of the relation of galvanometer deflection and maximum value of the alternating voltage; it is hoped that this may be carried out in the future.

The above experiment was suggested by Dr. J. A. Anderson.

This was almost anticipated by an experiment of Dr. J. B. Whitehead.[2] In 1911 he reported to the American Institute of Electrical Engineers his observations of the ionization due to alternating currents in the corona tube. The method used was this: A woven wire cylinder was the grounded electrode, and was surrounded by a solid cylinder of metal connected through a D'Arsonval galvanometer to a source of continuous potential, the other D.C. electrode being grounded. At start of corona an excess of positive ions reaches the detector; at higher alternating potentials the excess is of negative charges. This should be interpreted

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[1] Proceedings A. I. E. E., XXXII., 1473–1494, 1913.

[2] Ibid., XXX., 1857–1887, 1911.

to mean that the positive corona appears earlier, whereas when the negative corona is formed the ionization accompanying it is far more intense than that belonging to the positive half cycle. Dr. Whitehead, however, does not speak of the rectifying effect of the corona discharge: this would have been found had the galvanometer been in the A.C. circuit.

The theory of secondary ionization has been applied to the corona by Townsend.[1] His formula is verified by Watson's results. According to Townsend

$$kv = P\left(30 + \frac{9}{\sqrt{aP}}\right),$$

where P is the pressure in atmospheres and a the wire diameter.

An empirical law has been proposed by Peek[2] to comprehend the results of work on pressure and temperature. His equation is

$$g = 31\delta\left(1 + \frac{.3}{\sqrt{r\delta}}\right),$$

where g = critical surface intensity in kilovolts per cm.,

r = radius of wire,

δ = "density factor," $= 3.92p/(273 + t)$: p is the pressure in centimeters, t is the temperature centrigade.

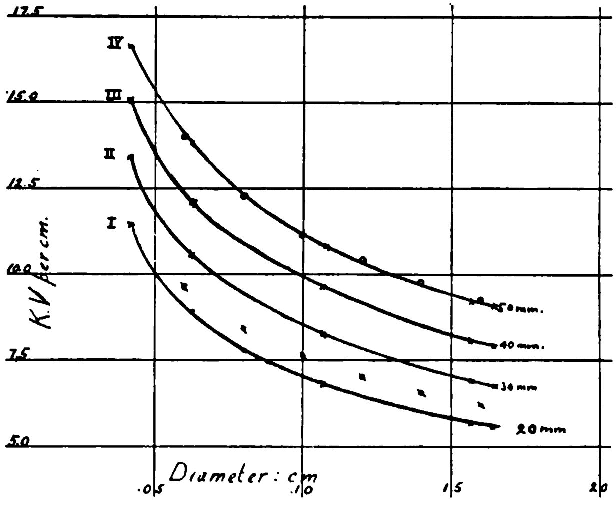

Fig. 4.

Critical surface-intensity and diameter of wire. Positive corona. Temp. = 21.°0 C. Circles indicate points plotted from Peck's law to compare with Curve III., δ = .0533, p = 4 cm.; crossed circles indicate points plotted from Peck's law to compare with Curve I., δ = .0267, p = 2 cm.

Electrician, *71*, 348, 1913.

[2] Proceedings A. I. E. E., XXX., 1889–1963, 1911; XXXI., 1051–1092, 1912; XXXII., 1337–1355, 1913.

On Fig. 4 are plotted points derived from this equation for $t = 21$ degrees and $p = 2$ cm. and 4 cm.

The comparison shows that the computed curves differ from the observed numerically but not in form—the difference being a function of the pressure but independent of the diameter of wire. Further observations are necessary to enable a suitable correction term to be determined.

Transition points at various pressures are shown in Fig. 5 for two wires. At the left in Fig. 5 is the curve of transition point for the positive corona, at the right that for the negative. The straight vertical lines in the positive figure represent the instantaneous drop in tube-wire voltage attendant upon the transition from corona to vacuum-tube discharge,—no such observations were made in the work on the negative corona. The ordinates of the upper curve are the voltages at which transition occurs; those of the lower curve are the voltages consumed by the vacuum-tube discharge immediately after the transition. The critical voltages are shown in dotted curves.

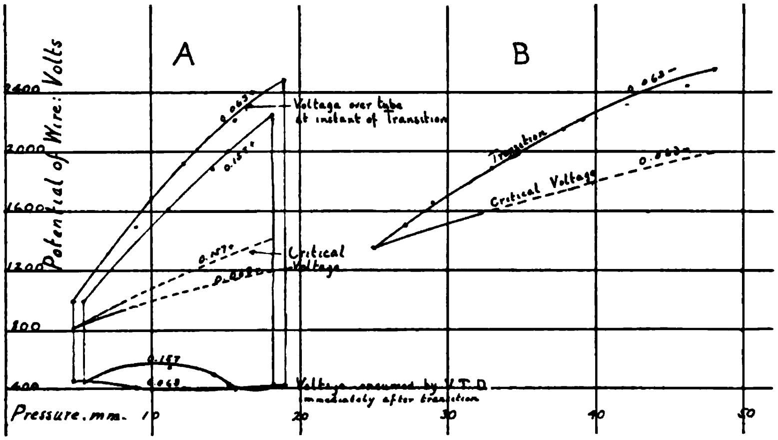

Fig. 5.

Voltage of transition from corona to vacuum-tube discharge. *A*, Positive effect, wires of diameter 0.157 cm. and 0.063 cm.; *B*, Negative effect, 0.063 cm. wire. Critical voltages shown in dotted curves.

In the case of the negative wire at pressure 24.5 mm. the curve of transition point intersects the curve of critical voltage. At this pressure the range of the negative corona on this wire is so narrow as to be within the voltage fluctuations. The observations do not establish such a point for the positive corona.

Conclusion.—It seems unprofitable to speculate on the nature of the corona until it has been more thoroughly studied. Observations at atmospheric pressure and at pressures considerably below the atmosphere have yielded empirical equations which require modification to enable them to include the results reported in this paper. The ionization current which in the case of small wires exists before the luminous discharge begins, the transition from corona to vacuum-tube discharge, the dependence of the stable negative corona on the wire size and on the pressure,—all these questions call for extended investigation.

The principal results of the work described in this paper may be briefly enumerated as follows:

1. The formation of the stable negative corona has been shown to be dependent upon the pressure and the size of conductor. Of the wires used, with those of larger diameter such a corona is never formed, while around the smaller wires the negative corona can exist only at pressures greater than a critical value which varies with the diameter of the wire.

2. The transition has been observed from the stable corona to the vacuum-tube discharge. The vacuum-tube discharge is the only luminous discharge with negative wires below the critical pressure.

3. Curves have been plotted of critical surface intensity for the positive corona and wire diameter at various pressures. These curves are similar in form to those of Peek's equation

$$g = 31\delta\left(1 + \frac{.3}{\sqrt{r\delta}}\right).$$

Values calculated from this equation differ from those observed by a quantity which is a function of the pressure but independent of the diameter of the wire. The observations are not sufficiently numerous to determine the correction to the formula.

4. The ratio of the critical voltages for the positive and negative coronas on a given wire varies with the pressure. A pressure exists at which the two critical voltages are equal; below this pressure the negative critical voltage is lower than the positive, at higher pressures the positive corona-forming voltage is the lower.

5. The corona rectifies an alternating current, the direction of the rectified current depending on the voltage and the pressure.

6. In the case of the smallest wire evidence has been found of the existence of an ionization current flowing before the appearance of the luminous discharge.

It is a pleasure to acknowledge the indebtedness I am under to those who have assisted me in this undertaking. The work was begun at the suggestion of Dr. J. B. Whitehead, and his published papers have been

constantly consulted. My particular thanks are due to Professor Ames, who has aided and encouraged the work in every possible way. Valuable assistance has been received from Dr. J. A. Anderson and Mr. M. W. Pullen. I am grateful as well to my fellow student, Mr. S. M. Burka, for his kindness in the matter of glass-blowing and to Mr. Frank Smith for his careful mechanical work.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, May, 1914.

ON THE EXTRACTION AND PURIFICATION OF RADIUM EMANATION.

By William Duane.

DURING the last few years a great many investigations have been made on the effects produced by relatively intense beams of Becquerel rays. The most efficient known sources of these rays consist of a small tube containing a considerable amount of radium emanation, or of a large deposit of radium *B* and *C* on a surface of small area. The author has constructed hundreds of such "radio-active lamps," at first for physical and chemical researches,[1] and more recently, in the laboratories of the Harvard Cancer Commission, for use in methods he has devised for investigating the therapeutic value of radio-activity in the treatment of cancers. The construction of these powerful sources of radiation requires the extraction of radium emanation from a great many milligrams of radium, its purification and its compression into small volumes. As many requests have been received for a description of the method employed, it does not seem out of place to publish the details of the apparatus.

The general principles of the method are those previously employed by Ramsay and Soddy, Rutherford, and Debierne,[2] in some of their most important researches. The advantages of the method described below are: that the purification does not require liquid air; that a large number of millicuries of emanation can be purified and compressed into a small fraction of a cubic millimeter, in ten or fifteen minutes of time; that no emanation is lost except that due to its natural decay; and that the process may be repeated a great many times without renewing parts of the apparatus.

Fig. 1 represents the arrangement of the glass tubes and reservoirs. The bulb *A* contains the radium salt dissolved in water. Radium in solution continually decomposes the water into hydrogen and oxygen, and at the same time transforms itself into the emanation, which is set free. The total volume of the hydrogen and oxygen amounts to more than

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[1] Comptes rendus, *153*, p. 336, July 31, 1911.

[2] For a brief description with references see Madam Curie, Traité de Radioactivité, Tome I., pp. 312–322.

two hundred thousand times that of the emanation at the same pressure and temperature.[1] In addition to the oxygen and hydrogen and emanation, a small quantity of helium appears (the volume of which is a few per cent. greater than that of the emanation) and also traces of other gases, probably carbon dioxide and hydrocarbons coming from the decomposition of organic impurities, although the source of these traces of gas does not seem to be thoroughly understood. On account of its radioactive transformation, the exact proportion between the quantity of emanation and the gases with which it is mixed, depends upon the length of time the gases are allowed to accumulate. In the ordinary daily routine of our laboratory, however, the problem resolves itself into the extraction of 35 to 60 millicuries of emanation having a volume of 0.021–0.036 mm^3. at atmospheric pressure and ordinary temperature, from a mixture of gases, having a volume of 4.5 to 9 c.c. at the same temperature and pressure.

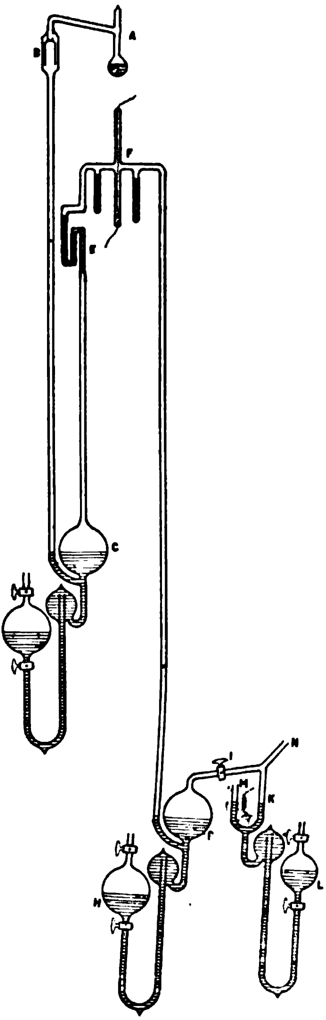

Fig. 1.

The mixture of gases collects in *A* and the tube *B*, and also, if the passage is open, in the reservoir *C*. Allowing the gases to collect in *C* apparently increases the efficiency, probably because the emanation defuses from the solution into a large volume more freely than into a small one. The tube *B* is considerably longer than 76 cm. so that air may be admitted into *C*, if desired, without its finding its way up to the radium solution. The trap at *B* protects against mercury spurting up into the radium solution, should some of the glass apparatus break. An ordinary water aspirator with suitable stop-cocks controls the flow of mercury between the reservoirs *C* and *D*. On admitting the air into *D*, the mercury rises in *C*, pushing the mixture of gases through the mercury trap *E*, into the tubes *F*. The mercury in the trap *E* holds back all but

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[1] Duane and Scheuer, Le radium, *10*, p. 33, 1913.

a very small quantity of the water vapor. The tubes *F* contain a copper wire slightly oxidized, phosphorpentoxide and potassium hydroxide. Although represented in the figure in a vertical position, the copper wire really lies horizontal. It is wound on a hard glass rod supported by glass feet, so that the wire does not touch the inner surface of the tube at any point. The diameter of the wire is 0.3 mm. and the length of the coil 25 cm. When heated red hot by an electric current of 5–10 amperes it rapidly combines the oxygen and hydrogen, the phosphorpentoxide absorbing the water vapor formed. A small amount of copper oxide on the wire is required, because the mixture of gases contains, at least at first, a quantity of hydrogen that exceeds by a few per cent. the proportion required by the chemical formula for water. Some oxygen remains in the radium solution as hydrogen peroxide. The copper wire was heated for a long time to remove as much of the occluded gases as possible, and the phosphorpentoxide was distilled into its present position from a tube sealed on just below it, and afterwards removed; both of these processes taking place in vacuum. The potassium hydroxide is for the purpose of absorbing any carbon dioxide that may be present, or may be formed by the hot copper wire oxidizing hydrocarbon gases.

After the purification of the emanation the mercury in the reservoir *G* is drawn into *H*, the air being removed from *H* by the water aspirator, and the emanation and helium pass into *G*. The gases are then pushed up by the mercury through the stop-cock *I* and into the desired tube or container, which is sealed on at *N*. The volume of the helium being very small, for the vast majority of purposes it is unnecessary to remove it. The length of the tube connecting *E* with *G* should be so great that air may be admitted into *G* without forcing the mercury up into *F*.

The stop-cock *I* has a mercury seal, and contains no stop-cock grease. A few marks made with a lead pencil on the stopper allow it to turn freely. It will be noticed that the emanation passes through no stop-cock except the one at *I*, and even this is unnecessary, and has been added for convenience of manipulation only. The fact that stop-cock grease and many other organic substances are decomposed by the rays from the emanation and give off gases is well known.

The system of tubes and bulbs *K*, *L*, *M* is for the purpose of removing the air from the other tubes and reservoirs, etc., by means of a pump attached at *M*. This must be done at the beginning, and after that no air enters the reservoirs except occasionally when it becomes necessary to renew the oxidized copper wire or the phosphorpentoxide, etc.

The apparatus in our laboratory has been in continuous daily use for more than eighteen months. The bulb *A* contains over two hundred and twenty milligrams of radium (element), and the total quantity of emanation purified per month amounts to slightly more than one curie of emanation, which is the quantity of emanation in equilibrium with one gram of radium (element).

Fig. 2 represents a few of the tubes and applicators used in investigating the effects produced by the Becquerel rays on cancers. The tiny glass tubes *A* contain radium emanation. They fit into the steel tubes just below them, which are provided with eyes and points as shown. While strongly active these tubes are used singly either with or without the silver jackets represented at *B*. The silver jackets act as filters, cutting off the easily absorbed rays. As the emanation disappears and the tubes become less active, a lot of them are placed together on flat applicators as at *C*. Thus each individual tube remains in use for over a month, at the expiration of which time the activity has fallen to less than one half per cent. of its initial value. *D* is a glass tube containing a thin sheet of metal. It illustrates the method of making deposited activity applicators, two of which are represented at *E*.

The glass bulbs *F* have been used to make highly radio-active solutions. The small bulb having been filled with common salt the tube is sealed on to the apparatus at *N*, Fig. 1, and the purified emanation is pushed up between the grains of salt, on which it deposits radium *AB* and *C*. On dissolving the salt in a small quantity of water a very active solution of deposited activity is obtained.

The advantages of using the emanation and deposited activity instead of the radium itself appear to be, (*a*) that the danger of losing the radium is reduced to a minimum, (*b*) that great flexibility as to the size, shape and strength of applicators, and penetration of rays may be obtained, and (*c*) that no large quantity of a radio-active substance of long life, such as radium, can become lodged by accident in the patient's body.

HARVARD UNIVERSITY.

PHYSISAL REVIEW, VOL. V., SECOND SERIES.
April, 1915.

PLATE I.
To face page 314.

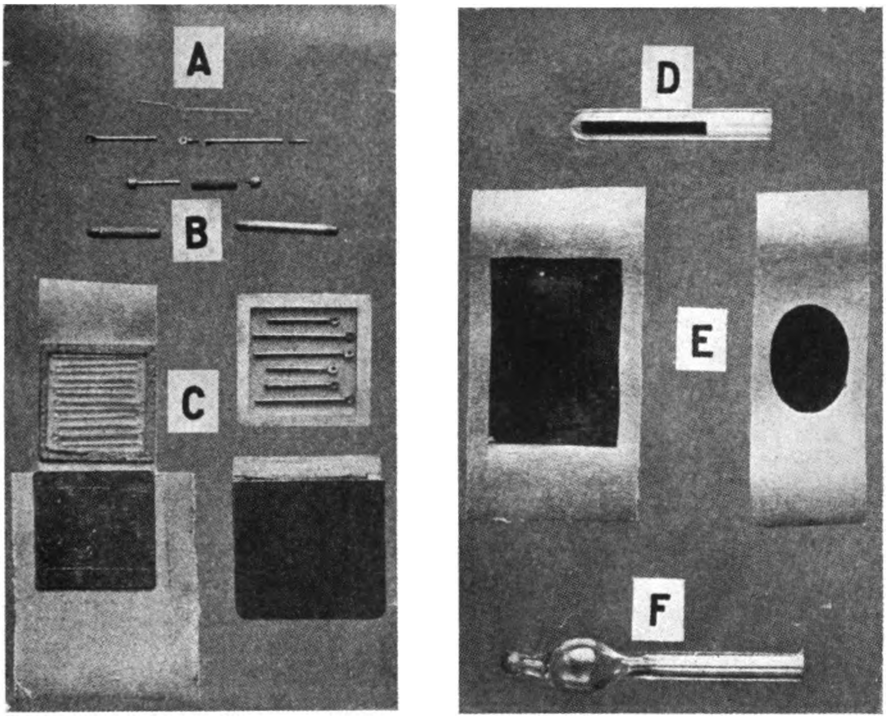

Fig. 2.

WILLIAM DUANE.

THE NATURE OF THE ULTIMATE MAGNETIC PARTICLE.

By K. T. Compton and E. A. Trousdale.

Introduction.—For many years scientists have agreed in ascribing the magnetic properties of bodies to the action of exceedingly small elementary magnets, but the nature of these ultimate magnetic particles has remained an open question. This theory in its earliest form was due to Weber, who supposed that the molecules of substances are magnetic doublets whose axes are arranged at random in the unmagnetized substance but, in opposition to restoring forces of elastic nature, are so directed by an external field that the substance acquires a definite resultant magnetic moment. Wiedemann suggested that the opposing couples are of a frictional nature, thus accounting for hysteresis but failing to explain magnetization in very weak external fields. Ewing then suggested that the only restraints on the molecules are due to the mutual magnetic forces occurring between neighboring molecules and showed that the residual magnetism and hysteresis of ferromagnetic substances may be thus accounted for. None of these theories accounted for diamagnetism. A development of Weber's theory, due to Ampère, is that the magnetic properties of molecules are caused by electric currents circulating about perfectly conducting circuits within the molecules. Maxwell showed that, when placed in an external magnetic field, the induced currents set up in these molecules would tend to oppose the field and thus give to the substance diamagnetic properties, while the change in the orientation of the molecular circuits would give rise to paramagnetic properties. Thus a substance is dia- or para-magnetic according as the former or the latter effect predominates.

With suitable modifications, Ampère's theory of molecular currents has been made the basis of the electron theory of magnetism, whose development is due largely to Langevin and Weiss. On this theory electrons revolving in orbits around the atomic nucleus give rise to magnetic fields and constitute the ultimate magnetic particles. In the presence of an external field the magnetic moments of the electron orbits are diminished in the direction of the external field by an effect analogous to electromagnetic induction, so that the resultant effect is of a diamagnetic nature. If the resultant magnetic moment of the electron orbits in each atom be different than zero, the planes of the orbits will be oriented so that the magnetic axis of each atom will tend to point in the direction of the external field. This gives rise to paramagnetism, whose intensity depends on the strength of the external field, the magnitude of the resultant magnetic moments of the atoms, the interatomic forces of electrostatic or other nature and the demagnetizing effect of the kinetic reactions due to thermal agitation. Ferromagnetic substances are those in which the resultant magnetic moments of the atoms are so large that all other interatomic forces are negligible in comparison.

A recent theory[1] suggests that certain numerical relations are most readily explained on the assumption that the ultimate magnetic particle is a natural unit, called the magneton. At present this must be regarded as a mere hypothesis, with a possible basis of fact, since its usefulness in explaining magnetic phenomena is limited to a very small number of phenomena.

The electron theory has been generally accepted as offering the most reasonable explanation of magnetic phenomena and is strongly supported by its success in accounting for the Zeeman effect. Yet there are several magnetic phenomena which apparently receive the readiest explanation on the molecular theory. The most significant of these are: (*a*) The influence of temperature, a molecular effect, on the magnetic properties of substances; (*b*) the effect of a changing magnetic field on the temperature, *i. e.*, on the average kinetic energy of the molecules of substances; (*c*) the effect of chemical combination, as in the case of iron salts and Heusler alloys; (*d*) the effect of mechanical jarring on the ease with which certain substances may be magnetized.

The recently developed method of determining the positions of atoms within a crystal by X-ray photography and the ferro-magnetic properties of magnetite, hematite and pyrrhotite crystals suggested a direct experimental method of eliminating one or the other of these theories. The magnetic properties of these crystals have been investigated by Weiss,[2] who found that these crystals may be magnetized strongly in the direction of each crystal axis, but that the degree and ease of magnetization is different along different axes. It is practically certain that the magnetic properties of iron and other substances are determined by the properties of the agglomeration of minute crystals of which they are composed. Thus the magnetic properties of crystals are typical of those of all magnetic substances.

We accordingly passed a beam of X-rays through crystals and obtained

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[1] Weiss, Le Radium, Vol. 8, p. 301, 1911.

[2] Journal de Physique, *3*, 5, p. 435, 1896; *4*, 4, p. 469, 1905.

on photographic plates the diffraction patterns which were determined by the arrangements of the atoms within the crystals. By comparing the photographs taken through the unmagnetized crystals with those taken through the same crystals when magnetized to various intensities it was possible to determine with certainty whether or not the atoms of a substance experience a translational displacement in the process of magnetization. We have found that no such motion occurs and hence that the molecular theory of magnetism, at least in its ordinary form, is untenable.

Apparatus and Method.—A powerful self-regulating X-ray bulb was enclosed in a lead box *EF* in such a position that a pencil *ab* of X-rays passed out through an opening *H*, through pin holes in the lead shields *LL'*, through the crystal *C* to the photographic plate *P*. The crystal was cemented by " Quixo " cement to one of the adjustable pole pieces *S* of an electromagnet capable of setting up a field of 1,000 gauss in the air gap. The other pole piece was prevented from touching the crystal in order to obviate the danger of a mechanical displacement of the crystal when strongly magnetized. The apparatus was enclosed in the light tight box *AD* with a removable back *B*. This box was made of sheet iron in order to reduce the effect of the magnetic field on the path of the cathode rays from *c* to *a*. Cramer X-ray plates, " New Process," were used, and the negatives were later intensified. The distance of the plate from the crystal was three inches and the exposures were for three hours.

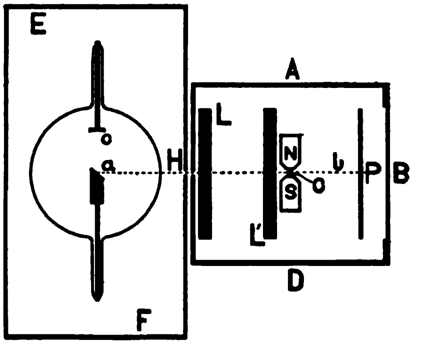

Fig. 1.

The procedure was to take a photograph through the unmagnetized crystal, then, without disturbing the crystal, turn on the current in the electromagnet and take a second photograph with the crystal magnetized, then take a third photograph with the direction of the magnetic field reversed and finally take another photograph with the crystal unmagnetized. This last photograph was a check to guard against possible effects due to any change in the position of the crystal. Supplementary experiments showed us that in every case the magnetic fields were of sufficient strength to strongly magnetize the crystal.

In this way a number of series of photographs were taken through crystals of magnetite and hematite variously oriented with respect to the magnetic field. In no case did we discover that magnetization influenced the diffraction pattern.

Two of these series of photographs, one taken with magnetite M and the other with hematite H, are shown in the accompanying figure. (*a*), (*b*), (*c*), (*d*) refer to the cases of the unmagnetized, magnetized, reversely magnetized and unmagnetized crystals. Unfortunately in bringing out the spots more clearly by intensifying the plates we did not succeed in strengthening the spots equally on the four plates. In the original negatives there was no difference in the cases (*a*), (*b*), (*c*), (*d*) either in the relative intensities or the positions of the spots. The "fogging" of several of the pictures is also due to the intensifier. We have not as yet succeeded in obtaining specimens of pyrrhotite crystals.

Discussion of Results.—These results show conclusively that the ultimate magnetic particles must be atoms or something within the atoms and are therefore consistent with the electron theory of magnetism. Doubtless a change in the orientation of an atom means the same thing as a change in the orientation of an electron orbit within the atom, since a turning of an electron orbit would upset the equilibrium of the remaining constituents of the atom so that the whole atom would change its orientation. However this may be, it is certain that the ultimate magnetic particle cannot be a molecule or other group of atoms, since the turning of such a system would involve a translational motion of atoms, which the present investigation shows does not exist.

PHYSICAL LABORATORY,
REED COLLEGE.

PHYSICAL REVIEW, VOL. V., SECOND SERIES.
April, 1915.

PLATE I.
To face page 318.

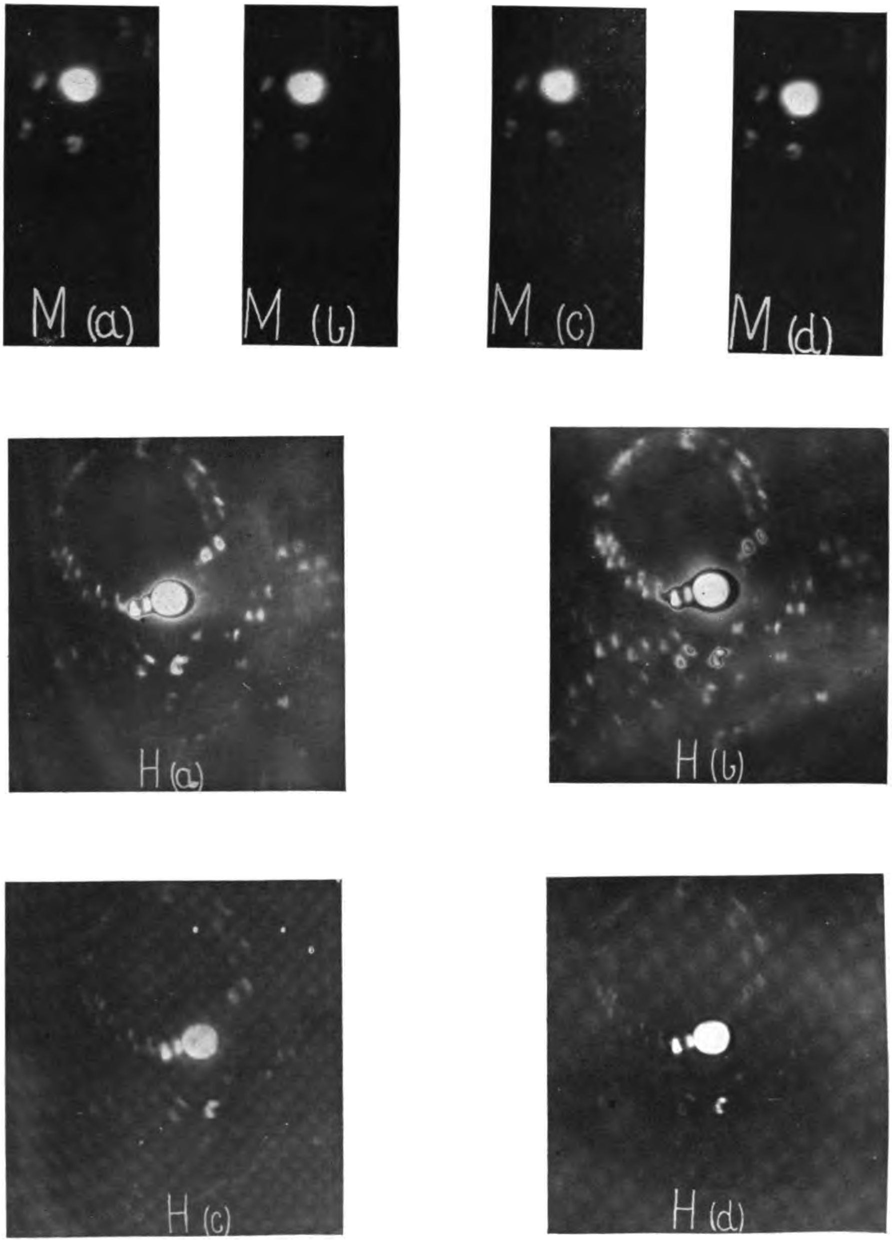

Fig. 2.

K. T. COMPTON AND E. A. TROUSDALE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

LUMINESCENCE.[1]

BY ERNEST MERRITT.

THE past twenty years have been remarkable in the history of physics on account of the large number of fundamental discoveries that have been made, each of which has opened up an entirely new field of investigation, and each of which has exerted a profound influence on the trend of speculation. I refer particularly to the discovery of X-rays and its modern development in the high frequency spectra, the discovery of the electron, and of radioactivity. But many other subjects of scarcely less importance might be included in the list; such, for example, as the photoelectric effect; and, on the theoretical side, the hypothesis of quanta. In each of these cases the original discovery not only appealed to physicists at once on account of its obvious importance, but possessed also the charm of complete unexpectedness. And in each case the subsequent development of the new subject was so rapid as to be almost spectacular.

In looking over the ground from our present point of advantage it is interesting to observe how these different subjects have supplemented one another, and how in some subconscious way we have been proceeding by seemingly accidental steps toward a definite goal,—toward the solution of the problem of the structure of the atom, which is now so generally recognized as the most important of the outstanding problems of our science.

On account of its important bearing upon this problem of atomic structure the subject of luminescence, in my opinion, deserves a place in the group of subjects just mentioned. In some respects, in fact, it offers a more direct line of attack than any of these. The chief purpose of my address to-day is, therefore, to make a plea for the more extended study of the phenomena and the theory of luminescence.

Luminescence is not a new subject. It cannot attract investigators by its novelty. If none of its phenomena were known, and if the phosphorescence of Sidot blende or the fluorescence of anthracene were to be shown at this

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[1] Presidential address delivered at the Philadelphia meeting of the Physical Society, December 29, 1914.

meeting for the first time, I am confident that half of this audience would be investigating luminescence within a week. But the first discovery was made three hundred years ago. The fascinating phenomena of luminescence have to a large extent lost the appeal of novelty, for in a superficial sort of way they are well known; but so far as the theoretical interpretation of the phenomena is concerned we have made only the barest beginning. The original discovery was made too soon—before the scientific world was ready for it. Important progress has indeed been made, especially on the experimental side; but it has been made slowly and with great effort. Until very recently the position of the subject has been like that of an isolated outpost of an army: it lacked support on the two wings. But the great advance of Physics during the past twenty years has at last furnished the much needed support, and it seems to me that the time has come for the outpost to advance.

Having in mind the general question of the bearing of the phenomena of luminescence upon the problem of atomic and molecular structure, the various subdivisions of our subject may be roughly grouped in two classes. The first class includes such subjects as phosphorescence, chemiluminescence, and the influence of temperature upon these phenomena. The interpretation of the phenomena of this class involves a consideration of the relations between molecules, but does not necessarily require any hypothesis regarding the mechanism by which the light is actually emitted. We have a somewhat analogous case in the subject of magnetism, where important progress was made by the assumption that each molecule is a magnet, even before any serious attempt was made to explain the peculiarities of molecular structure to which the assumed magnetic property was due.

The second class of subjects, which bears more directly upon the problem of atomic structure, includes such matters as the detailed study of luminescence spectra, the relations between luminescence and absorption, and the influence of the wave-length of the exciting light, or more generally the influence of the mode of excitation, upon the character of the light emitted. No progress toward a theoretical interpretation is possible in these cases without some hypothesis regarding the mechanism of emission and absorption. I need hardly point out that it is often difficult, if not impossible, to entirely separate the two classes of problems.

As an illustration of important progress made by purely empirical experimentation, without the help of even the crudest theory, we have the development of the methods now used in preparing phosphorescent materials artificially. In the early days the results of attempts to make phosphorescent materials were very uncertain. Preparations made by the same method and from the same materials were in some cases brilliantly phosphorescent and in other cases entirely inactive. The color of the phosphorescence and its duration also seemed to be largely a matter of chance. An important step toward an understanding of the reasons for these uncertainties was taken by Lecoq,[1]

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[1] See Kayser, Handbuch der Spectroscopie, Vol. IV., p. 741. The chapters on Phosphorescence and Fluorescence in Kayser's Handbuch contain so complete and valuable a

who was led to believe that in most cases phosphorescence was due to the presence of impurities. Thus $CaSO_4$ gives very weak phosphorescence and $MnSO_4$ none. But if we mix the two we get a mixture which is brilliantly phosphorescent. Lecoq was the first also to suggest that phosphorescent substances were to be looked upon as solid solutions, a view which is now very generally accepted. Thus Sidot blende consists of a small amount of copper or manganese dissolved in zinc sulphide. Balmain's paint is a solid solution of bismuth in calcium sulphide. The usual method of preparation is by the calcination of the mixed dry salts.

Lecoq's views were confirmed by Verneuil, who found that better results were obtained if a flux such as NaCl or Na_2CO_3 was used. More recently Lenard and Klatt have developed the procedure in the case of the metallic sulphides in great detail, so that if we have pure materials to start with we are now in a position to reproduce the phosphorescent preparations of this class with considerable certainty.

Wiedemann and Schmidt have used two other methods of preparation, which, while probably not so generally applicable, sometimes have the advantage of not requiring calcination. One of these methods simply calls for the evaporation to dryness of a suitable mixture of two salts. For example, if a small amount of a solution of $MnCl_2$ is added to a solution of NaCl and the mixture evaporated to dryness, the dry salt gives a pink phosphorescence.[1] In some cases the precipitation of a metal from a solution will carry down a sufficiently large amount of some other metal present to give the proper conditions for phosphorescence in the dried precipitate.

In all these cases the essential thing seems to be the bringing into intimate association of a small amount of one substance—usually called the active substance—and a large amount of some other substance, the latter acting as the solvent in the resulting solid solution. The intensity of phosphorescence is found to vary greatly with the concentration, increasing rapidly with the concentration at first and, after reaching a sharply defined maximum, decreasing scarcely less rapidly as the amount of active material is still further increased. In the case of the solid solution of $MgCl_2$ cited above the maximum is reached for a concentration of 0.8 per cent. The sulphides studied by Lenard and Klatt usually give maximum brightness with a concentration of .01 per cent. or less.

In cases where so small an amount of active substance is required for brilliant results it is evident that the purity of the materials used is a matter of great importance. It is very difficult to obtain a salt which is sufficiently pure to be entirely free from phosphorescence, especially when tested by cathode rays. The extreme sensitiveness of certain substances to small traces of impurity is illustrated by an experience described by Waggoner.[1] After a long search

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discussion of the literature down to the date of publication (1908) that I have usually not thought it necessary to cite references except in the case of work done since that date.

[1] C. W. Waggoner, Phys. Rev., XXVII., p. 209.

some cadmium sulphate had been obtained which showed only the barest trace of afterglow. This was dissolved in water that had been twice distilled, but which had stood in a glass bottle over night. When the solution was evaporated to dryness the salt was found to be brilliantly phosphorescent. The water had evidently dissolved some substance from the glass of the bottle in which it had been kept. But when 200 c.c. of the water from the same bottle was evaporated in a platinum vessel it left a residue so small that it could be seen only when the vessel was at a red heat. There are many evidences that phosphorescence may often give a test of purity which is equalled in sensitiveness only by spectroscopic examination, or by the ionization test for radium.

That luminescence in minerals is also due to impurities has been definitely proved in a large number of cases. Probably we all recall the important assistance that was given by kathodo-luminescence in the study, and in some instances the discovery, of several of the rare earths. The opinion is now generally held that impurities are present in the great majority of cases of luminescence in solids, possibly in all cases. Yet there does seem to be one exception, namely the salts of uranium. The presence of slight impurities in these salts is of course probable. But their fluorescence seems to be chiefly determined by the uranyl radical, and retains the same general character whatever may be the acid with which this radical is combined or the source of the uranium. This exception to the general rule is so striking that I have sometimes wondered whether the active substance in this case may not be one of the radio-active products of uranium, for which the salt serves as a solvent. A few experiments have been made to test this conjecture. For example the salt has been freed from Ur-X in the hope that it would lose its fluorescence thereby until new Ur-X was formed. But the results are thus far altogether negative.

On the whole very satisfactory progress has been made in developing methods of preparing phosphorescent materials. And yet we can scarcely feel content, for the knowledge gained is almost entirely empirical. We have no means of telling what substances may be used to advantage either as solvents or as active substances—except, of course, that certain materials have been tried before and have been found to work. The fact that phosphorescent substances are in most cases solid solutions is virtually the only generalization that can be used as a guide.

In some of the other problems of luminescence the situation is better, for a suggestion first made by Wiedemann in 1889 and since resuggested in more or less modified form by several other physicists, has proved of great utility. According to the Wiedemann theory luminescence is an accompaniment of what the chemists would call, I believe, a reversible reaction. It is assumed that the active substance is changed by the action of the exciting agency from the stable condition A into the unstable condition B. If the return of the substance to the condition A is accompanied by the emission of light we have phosphorescence. Fluorescence may be due either to vibrations set up during the change from A to B, or to the fact that the reaction B to A proceeds, with the emission of light, during excitation as well as during decay. We should expect, therefore, that the fluorescent light, that is the light emitted during excitation, would consist in part of the same wave-lengths that are present during phosphorescence, but that other wave-lengths, resulting from the reaction A to B, may also be present and in some cases predominant. An explanation is thus offered of the fact that the color of phosphorescence is often different from that of the fluorescence of the same substance with the same excitation. Thermo-luminescence is to be explained as the result of some change that is made possible by rise of temperature, during the progress of which the molecules are thrown into such violent vibrations as to emit light. In many instances thermo-luminescence seems to be nothing more than accelerated phosphorescence. In such cases the conditions at the temperature of excitation are apparently not favorable for the rapid emission of the energy stored during excitation. Phosphorescence is therefore very weak and of extremely long duration. This may be true in so marked degree that no phosphorescence can be detected at all, and the condition produced by excitation is practically permanent so long as the physical conditions remain the same. In such cases the reaction A to B can occur at the lower temperature, while the reverse reaction B to A cannot. But if the temperature is raised it becomes possible for the stored energy to be liberated and thermo-luminescence is observed. In such cases the material will not show thermo-luminescence when heated a second time until it has been reexcited, say by the light of a spark or by cathode bombardment. If all cases of thermo-luminescence are of this kind we should not expect thermo-luminescence to be shown unless there has at some time been an opportunity for excitation. In the case of certain natural minerals whose freshly exposed surfaces were found to show thermo-luminescence even when the specimen had been broken in the dark, it has been suggested that the original excitation was due to radium rays.

The theory illustrated by these few examples was first advanced by Wiedemann in his well known paper entitled "Zur Mechanik des Leuchtens."[1] It was discussed in much greater detail in a later paper by Wiedemann and Schmidt,[2] which appeared in 1895, and which in my opinion is to be regarded as one of the classics in the field of luminescence.

While the fundamental conception of the Wiedemann theory has been retained, it has been customary in recent years to make the hypothesis more definite by assuming that the change which I have referred to as the reaction A to B consists in the expulsion of an electron from a molecule of the active substance, while the recombination of the ions thus formed constitutes the reverse reaction B to A. This is the form of the theory that has been advocated by Stark, Lenard and others. Chemists I believe are still inclined to look upon the change assumed in the Wiedemann theory as a chemical reaction in the ordinary sense. My own feeling is that we must admit the existence of several distinct types of luminescence, in some of which the phenomena are

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[1] E. Wiedemann, Annalen der Physik, 37, p. 177, 1889.

[2] E. Wiedemann and C. C. Schmidt, Annalen der Physik, 56, p. 177, 1895.

explainable in terms of electron dissociation alone, while in others chemical changes form the predominant factor. Although it may later be possible to bring all cases of luminescence into one category as regards the process which leads to the emission of light, I doubt whether we are yet in a position to do this.

In support of the Wiedemann theory in its general form we have several well established facts. For example when fluorescence is excited in liquids or in isotropic solids the light emitted is unpolarized, regardless of the condition, as regards polarization, of the exciting light. Apparent exceptions are noticed when the fluorescent surface is observed at an oblique angle, since the light from the interior is partially polarized by refraction when it passes into the air. But a study of such cases by Millikan has shown that there is nothing to indicate any polarization in the light before it reaches the refracting surface. The absence of polarization is one of the strongest arguments against any theory which assumes that the vibrations causing emission are set up by some process analogous to resonance. On the other hand it is just what we should expect from the Wiedemann theory, since the light emitted during the change B to A cannot be affected by the manner in which the condition B was established. The argument is equally strong whether the process B to A consists in the recombination of ions or in a chemical reaction. In the case of the fluorescence of vapors, Wood has found that the fluorescence light is partially polarized.[1] This fact offers support to the view that the processes of excitation and emission are essentially different from the corresponding processes in solids and liquids, and justifies the term resonance radiation which Wood has applied to this type of fluorescence.

Experiments made with excitation by light of different wave-lengths, by X-rays, and by cathode bombardment indicate that the distribution of energy in a fluorescence spectrum is the same for all of these modes of excitation.[2] It often happens that not all of these exciting agencies are effective; or that the substance tested possesses several independent fluorescence bands, which are excited by the different agencies to a different extent. In such cases the color of the total light emitted may vary with the mode of excitation. But if we direct our attention to some one band it is found that if this band is excited at all the distribution of intensity throughout the band is the same for all modes of excitation thus far tested. This result is of course what the Wiedemann theory would lead us to expect, for the phenomena connected with the change from the condition B to the condition A will not depend upon the means by which the change from A to B was produced. Or, speaking in terms of the modern form of the theory, the effects produced when an electron reunites with the positive nucleus will be the same no matter what method was used in bringing about its dissociation.

Similar reasoning based on the Wiedemann theory would lead us to expect that the distribution of energy in a phosphorescence band will remain the same throughout the period of decay. On account of the faintness of phosphores-

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[1] R. W. Wood, Philosophical Magazine, 26, p. 846, 1913.

[2] E. L. Nichols and E. Merritt, PHYS. REV., XXVIII., p. 349.

cence spectra this conclusion is difficult to test with any high degree of accuracy; but in so far as it has been possible to test it the conclusion is confirmed.[1]

Studies of the law of decay of phosphorescence, while leading in many cases to confusing and even contradictory results, on the whole lend support to the Wiedemann theory. If the exciting light produces a separation of the active material into two parts—and if this is its only effect—then we should expect the recombination to occur in accordance with the laws that apply to bimolecular reactions. It can readily be shown that in this case the law of decay should be

$$I = 1/(a + bt)^2 \quad \text{or} \quad 1/\sqrt{I} = a + bt$$

where I is the intensity of phosphorescence at any time t.[2] The law can be conveniently tested by plotting the reciprocal of the square root of I against t, in which case, if the law is obeyed, a straight line is obtained.

In the case of the afterglow in gases Trowbridge has found this law to hold with great exactness.[3] It also applied during the early stages of decay in the case of a number of solids, for example in the case of Sidot blende. Usually, however, when $I^{-1/2}$ is plotted against t the resulting curve is found to consist of two parts, each of which is nearly straight, separated by a region of rather sharp curvature.[4] Such curves suggest that the decay involves two processes, which have been called by Lenard the Momentan-prozess and the Dauer-prozess, the former being predominant during the early stages of decay and the latter during the period of slow decay which follows. In Lenard's experiments the first or Momentan-prozess has been found to follow a law of the exponential type.

Ives and Luckiesch[5] have found that in some cases even the second process does not give a linear relation, but shows considerable curvature, sometimes curving up and sometimes down.

The question of the decay of phosphorescence is complicated by two considerations, both of which are neglected in the derivation of the simple linear law. In the first place phosphorescent solids are very far from being homogeneous, and it has been shown that lack of homogeneity is in itself sufficient to account for most of the observed deviations from the simple law.[6] In the second place we have no reason to feel sure that a separation of the active material into two parts is the only effect of excitation. Secondary changes, possibly chemical in their nature, may in many cases follow this primary change. Both of these disturbing factors may perhaps be removed by working at low temperatures.

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[1] E. L. Nichols and E. Merritt, Phys. Rev., XXI., p. 247, 1905; C. W. Waggoner, Phys. Rev., XXVII., p. 220; C. A. Pierce, Phys. Rev., XXX., p. 663, XXXII., p. 115; H. E. Ives and M. Luckiesch, Astrophysical Journal, XXXIV., Oct., 1911.

[2] E. L. Nichols and E. Merritt, Phys. Rev., XXII., p. 279, 1906.

[3] C. C. Trowbridge, Phys. Rev., XXVI., p. 515; XXXII., p. 129.

[4] E. L. Nichols and E. Merritt, Carnegie Publication, No. 152.

[5] H. E. Ives and M. Luckiesh, Astrophysical Journal, Vol. XXXVI., p. 330, 1912.

[6] E. L. Nichols and E. Merritt, Carnegie Publication, No. 152, Chapter XV.

At the temperature of liquid air secondary chemical changes could scarcely occur. While if an amorphous phosphorescent substance is formed by freezing a homogeneous solution we should expect that the material would be approximately homogeneous. Experiments along this line by Kennard[1] are encouraging, since in the case of paraffin and frozen kerosene the decay, at the temperature of liquid air, was found to follow the linear law.

The study of phosphorescence is also complicated by the fact that in many substances the effect produced by a given excitation is largely affected by the previous history of the specimen. After a substance has been excited and then allowed to decay until no trace of phosphorescence can be detected its condition is usually not the same as it was originally. If subjected for a second time to the same excitation, even after a rest of several days, its phosphorescence is found to be brighter and of longer duration. In many cases also the substance is found to be thermo-luminescent. In studying the decay of phosphorescence this residual change must be taken account of, and in the more recent work the substance has usually been brought back to a standard condition by heating, or by brief exposure to infra-red radiation. But the cause of the residual change and the methods for its removal are so little understood that we cannot feel at all certain that the disturbances due to it are really eliminated.

Another source of disturbance,—which is at the same time a very interesting phenomenon in itself—is the effect of the red and infra-red rays upon the decay of phosphorescence. In the case of Balmain's paint the longer rays cause a considerable increase in the brightness of phosphorescence, which, however, is only temporary and is followed by more rapid decay. In Sidot blende it has usually been thought that the effect is simply to increase the rapidity of decay without any preliminary increase in brightness. But Ives and Luckiesch[1] have found that while this is true during the early stages of decay, a temporary flashing up of phosphorescence can also be observed in Sidot blende if the exposure to infra-red takes place after the decay has proceeded for several minutes.

It is clear that the phenomena of phosphorescence are extremely complex. And unfortunately the complexity appears to be especially great in the case of the substances that are most common and therefore most frequently studied. The problem has not yet been reduced to its lowest terms. In the further study of the subject it appears to me of the greatest importance to choose the conditions of observation, if this is possible, so as to eliminate some of the sources of disturbance. The work of Kennard[2] at low temperatures appears to be a promising step in this direction.

Let us consider now the problems of luminescence which are more obviously and directly connected with the question of atomic structure. Take for example the question of the relation between the wave-length of the exciting light in the case of fluorescence or phosphorescence and that of the light emitted.

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[1] Kennard, E. H., PHYSICAL REVIEW, IV., p. 278, 1914.

[1] Ives and Luckiesch, Astrophysical Journal, Vol. XXXIV., p. 173, 1911.

[2] Kennard, E. H., PHYSICAL REVIEW, IV., p. 278, 1914.

Since excitation cannot occur without absorption this question is closely connected with that of the relation between the luminescence spectrum of a substance and its absorption spectrum.

The law, first enunciated by Stokes, that the wave-length of the fluorescent light is always longer than that of the exciting light has led to extended discussion and experiment. Probably more papers have been published dealing with Stokes' law than on any other topic connected with luminescence. The fact that there are many cases where the law is violated seems to be now well established. The most striking exceptions to the law are probably those found by Wood in the case of fluorescent vapors. But even in these cases the longest wave-length that will excite luminescence is only a little longer than the shortest wave-length in the light emitted. As a general statement of what appears to be a fundamental relation the law still retains its value.

For a long time Stokes' law was thought to be exact, and attempts were made to base it upon thermodynamic reasoning. Fluorescence was thought of as a case of degradation of energy, the transformation of the short wave energy of the exciting light into the long wave energy of fluorescence being looked upon as somewhat analogous to the passage of heat from higher to lower temperature. I think that the attempts to base Stokes' Law on the Second Law of Thermodynamics are now generally regarded as unsound. Nevertheless this view has many attractive features, and it does not seem to me that it should be finally dismissed until, with the aid of the more recent methods of thermodynamics, it has been again considered.

Another explanation of Stokes' law has been based upon the theory of quanta. If excitation is due to the emission of electrons under the influence of the exciting light, in other words to a process analogous to that of the ordinary photoelectric effect—the velocity with which the electron leaves the active molecule will be determined by the wave-length of the exciting light. Similarly the wave-length of the light emitted when the electron returns will be determined by its energy at the time of recombination. Owing to collision with other molecules, however, a portion of the energy of the electron will generally be lost before an opportunity for recombination occurs. On the whole, therefore, the frequency of the light emitted will be less than that of the exciting light. This explanation has the advantage of accounting for the deviations from Stokes' law, for there will always be some electrons, although relatively a small number, which gain energy by collision before returning, and the light emitted during recombination will in such cases have a shorter wave-length than the exciting light. This view leads us to expect also that the deviations from Stokes' law will be less marked at low temperatures; and the small number of experiments which bear upon this question are in agreement with the theory. This explanation of Stokes' law, which is due to Einstein, is interesting in being almost the only case in which the theory of quanta has been applied to luminescence.

In the case of solids and liquids the fluorescence spectrum usually consists of one or more bands, shaded in both directions from a well defined maximum, and rarely less than one or two hundred Ångström units in width. In some cases the band may extend nearly throughout the visible region. In a large class of cases, but apparently not in all, the region of most intense excitation is immediately adjacent to the fluorescence band, on the short wave side. This region of excitation corresponds, of course, to a region of absorption; and in a large class of substances, of which fluorescein and eosin are typical, a certain symmetry is noticeable when we compare the curve of intensity in the fluorescence spectrum with the curve which gives the absorption coefficient as a function of wave-length. The fluorescence curve is steep on the short wave side and dies away gradually toward the red; while the absorption curve is steep on the long wave side and dies away gradually toward the violet. In cases where the two curves overlap, and this is usually the case, Stokes' law is violated.

Although the region of maximum excitation occupies the position just described, the substance is usually excited to some extent also by light of shorter wave-lengths. This fact is very beautifully illustrated by throwing a spectrum from a quartz prism upon the surface of a solution of one of the fluorescent dyes, such as fluorescein. The brightness of the fluorescence excited by the relatively weak ultra-violet rays is often such as to suggest that the energy of the light is more efficiently utilized for excitation when in the form of short waves. There has been no experimental test of this conjecture in the case of ultra-violet excitation. But throughout the principal absorption band the reverse has been found to be true.[1] The specific exciting power, that is the fluorescence excited by a given amount of absorbed energy, is greater for light at the long wave side of the band than in the middle, and still greater than for light on the violet side. I am inclined to think that we have here a promising case for the application of the theory of quanta, which by the aid of plausible hypotheses may be made to give at least a qualitative explanation of the facts.

While most substances possess a luminescence spectrum in which the bands are few in number and quite broad there are several exceptions, and the number of exceptions is increasing as the study of luminescence proceeds. In the case of anthracene there are four or five bands, which are narrow even at ordinary temperatures and become quite narrow as the temperature is lowered. A still more notable case is that furnished by the uranium salts, which have played so important a part in the history of luminescence as well as in the history of radioactivity.

The fluorescence of these salts is not only remarkable because of its brilliancy, but still more so on account of the structure of its spectrum, the manner in which the energy is distributed among the different bands, and the striking and significant relation that is found to exist between fluorescence and absorption. Brilliant fluorescence is shown only in the uranyl salts, *i. e.*, the salts in which the uranium occurs in the radical UO_2. At ordinary temperatures seven or eight bands are usually visible, the width of each being in the neighborhood of 100 Ångström units. Although the different uranyl salts give bands which differ

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[1] E. L. Nichols and E. Merritt, Carnegie Publication, No. 152, Chapter XIII.

somewhat in position and width the general appearance of the spectrum is much the same in all cases. The absorption spectrum of these salts also consists of a group of bands, whose width is approximately the same as that of the fluorescence bands. If plotted on the scale of frequencies the bands are found to be spaced at equal intervals, the absorption bands apparently forming a continuation of the bands of fluorescence as we proceed toward the shorter waves. It is found, however, that the regions of fluorescence and of absorption overlap, and that the bands which are common to both regions are "reversible." That is to say these bands will appear as absorption bands if the substance is observed by transmission in white light, but will appear as fluorescence bands if the substance is illuminated by ultra-violet rays only.

If we measure the intensity of the successive bands, starting with the band in the red, we find that the energy increases from band to band until a maximum is reached for a band lying in the green, after which the intensity for each succeeding band is much less than that of the one that precedes it. The distribution of energy in each band as determined by the spectrophotometer is much the same, on a small scale, as the distribution among the bands. Curves plotted to show the distribution of energy in a single band, in the group of bands, in the fluorescence band of a substance like fluorescein, and in the spectrum of a black body, are of the same type, and so strikingly similar in form that we might pass from one to the other simply by changing the wave-length scale.[1] At low temperatures each band of the uranyl spectrum breaks up into a group of lines, and I do not doubt that if the energy distribution in each line could be determined it too would be found to give a curve of the same type. One is reminded by this group of curves of an old rhyme, whose origin I do not recall, but which finds its applications in physics as well as in entomology:

The very fleas have other fleas,
And lesser ones, to bite 'em
And these again have other fleas;
And so *ad infinitum.*

Upon looking at these curves one can scarcely escape the feeling that both the fluorescence and the absorption regions in a substance like fluorescein are really made up of bands like those in the uranyl salts, but that the bands are so broad as to overlap and form single bands of fluorescence and absorption respectively, which we are unable to resolve.

At the temperature of liquid air both the fluorescence and absorption of the uranyl salts become more complex. Each fluorescence band breaks up into several extremely narrow bands, which are often as sharp as spectral lines; and new lines frequently appear in the regions that were dark at higher temperatures. In the absorption region also the bands are replaced by lines. In general appearance and in complexity these spectra suggest the spectra obtained from an arc or from a vacuum tube. They are in reality, however, much simpler, since it is possible to arrange the lines in groups or series, in

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[1] E. L. Nichols and E. Merritt, Phys. Rev., XXXIII., p. 354, 1911.

each of which the lines are spaced at equal intervals on the scale of frequencies. It often happens that the absorption lines can be most satisfactorily arranged in series for which the interval is shorter than that of the fluorescence bands. But in some cases the fluorescence series appear to be continuous with the absorption series, with the interval constant throughout, and with certain lines capable of appearing either as fluorescence or as absorption according to the method of observation.[1]

It is natural to expect that it would be possible, by a suitable choice of the exciting light, to excite one series of fluorescence lines without exciting the rest. As yet, however, no one has succeeded in doing this, although some slight indications have been found that the intensities of the different series do not change in exactly the same ratio as the excitation is changed. Light corresponding to one of the absorption bands is undoubtedly more effective in excitation than that falling in the intervals between bands. But diffuse absorption which is capable of producing excitation is present throughout the short wave region, so that any light lying on the short wave side of the first reversible band is able to excite to some extent. The whole question of the relation between the wave-length of the exciting light and the intensity and structure of the fluorescence spectrum requires further study.

In some respects the most promising field for study in the whole subject of luminescence is that opened up by Wood[2] in his work on the fluorescence or resonance spectra of vapors. Unfortunately the experimental difficulties are so great that few physicists have had the courage to undertake the work. The vapors of sodium, potassium, iodine and many other elements show fluorescence spectra consisting of a vast number of lines, so narrow that these spectra will stand analysis by the most powerful methods of spectroscopy. The absorption spectra of such vapors are equally complex. Wood estimates that the absorption spectrum of iodine contains not less than 35,000 lines in the visible region. The complexity of the phenomena would be altogether disheartening if it were not for the fact that the fluorescence can be greatly simplified by the use of monochromatic light for excitation. If a single line of some strong gaseous spectrum is used for excitation the fluorescence spectrum is found to consist of a relatively small number of regularly spaced lines. At first Wood was of the opinion that each of these fluorescence lines corresponded in position to a line in the absorption spectrum. His more recent work shows, however, that this is not in all cases true.

The lines of a given series, although spaced with great regularity, do not show constant intervals, either on the scale of frequencies or on that of wave-lengths. If plotted to a frequency scale the intervals increase slightly as we pass toward the shorter wave-lengths. In this respect therefore the series are not as simple as the constant interval series of the uranyl salts. It must remembered, however, that Wood has pushed his resolving power much further than would be possible with the uranyl spectra. If the latter could be resolved to the same

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[1] H. and J. Becquerel and H. K. Onnes, Leiden Communications, No. 110, 1909.

[2] R. W. Wood, Philosophical Magazine, 24, 673, 1912; 26, p. 828, 1913.

extent and measured with the same accuracy as was reached by Wood in the study of iodine it is not at all unlikely that variations from the constant interval law could be detected.[1]

It will be noticed that there is a striking resemblance between the fluorescence spectra of the uranyl salts when these are observed at low temperatures, and the resonance spectra of vapors,—a resemblance which is the more remarkable when we remember the widely different conditions under which emission occurs in the two cases. In neither case, unfortunately, has experiment gone far enough to make sure that the resemblance is more than superficial. In vapors the resonance bands appear to be closely connected in many cases with the ability of the vapor to rotate the plane of polarization in a magnetic field. In the case of the uranyl salts the magnetic rotation has not been tested. On the other hand in the case of vapors the relation between fluorescence and absorption has not yet been definitely determined so that we are not in a position to say either that the vapors show the same remarkable relation between these phenomena that is so characteristic of the uranyl salts, or that the relation is an entirely different one. To my mind it is a matter of considerable importance to determine whether the phenomena of fluorescence really are essentially the same in these two widely different cases. It has already been pointed out that the ordinary cases of fluorescence like that of eosin may be looked upon as being of the same type as the fluorescence of the uranyl salts, apparently the only difference being that the bands are so broad that they fuse together to form a single band of fluorescence and a single band of absorption. If now it should turn out that the fluorescence of vapors is also of the same type we should be justified in concluding that the fundamental processes involved in fluorescence are the same in all cases.

The study of the fluorescence of rarefied vapors and the study of low temperature fluorescence of solids like the salts of uranyl represent to my mind two attempts, along radically different lines, to simplify the conditions under which emission is caused to occur. In the case of vapors collisions occur only rarely, but when they do occur the disturbing effect upon the process of emission must be of considerable importance. In the low temperature fluorescence of solids each radiating molecule is closely surrounded by other molecules all the time and its vibrations are doubtless in consequence greatly modified. But on the other hand the molecular movements due to temperature are relatively sluggish; and collisions between molecules are far less violent than at higher temperatures; possibly at sufficiently low temperatures, especially in crystals, the molecular movements are reduced to vibrations about a position of equilibrium, with no collisions at all. The experimenter has his choice between a molecule which is

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[1] In the measurements of H. and J. Becquerel and H. K. Onnes (Leiden Communications, No. 110, 1909) there is some indication of an increasing interval as we pass toward higher frequencies. In some cases successive intervals differed by as much as 0.1 per cent. In the resonance spectra of sodium each interval is on the average about 2 per cent. greater than the preceding and in iodine 5 per cent.

subjected to large but nearly constant disturbing forces and one which, while ideally free from disturbance most of the time, is obliged to pay for this immunity by occasional periods of extremely great disturbance. I must confess that my preference is for the slow and plodding molecule, in spite of the fact that he is usually found in a crowd. It may be, however, that it will prove possible to combine the advantages of the two methods. If resonance radiation should be discovered in hydrogen or helium for example, or even in oxygen or nitrogen, these gases might be studied in rarefied form at low temperatures, and almost all sources of disturbance would be removed.

It is through the further study of the line spectra of luminescence, of which the resonance spectra of the vapors and the fluorescence spectra of the uranyl salts are typical examples, that I think we may expect the subject of luminescence to contribute most directly to the solution of the problem of atomic structure. Personally I feel that such study offers a more promising line of attack than any other that is now open to us, not excepting even the study of radioactivity or of the X-ray spectra.

Of course I cannot expect this view to be accepted without challenge. In the early days of spectroscopy there was a very general belief that the study of line spectra would enable us to determine the mechanism of emission, and therefore the structure of the radiating atom, in much the same way that we might hope to determine the nature of a sounding body from a study of the relations among its overtones. But the results have been disappointing, and physicists are not nearly so optimistic as they were. Now the subject of luminescence, in so far as it concerns itself with the study of luminescence spectra, is merely a branch of spectroscopy. In fact, if we use the term luminescence in its broadest sense, the greater part of the whole subject of radiation would probably fall under this head. Why should we expect the study of fluorescence spectra to offer more promise than the study of flame or arc spectra? The question becomes more pertinent when we remember that the spectra studied by Wood are as rich in lines and as complicated as arc spectra, while the experimental difficulties are much greater. Again, the resonance spectra and the uranyl spectra resemble closely the band spectra of ordinary spectroscopy; which, with their thousands of closely crowded lines, form a maze of such complexity that only a few spectroscopists have cared to attack them.

The strong argument in favor of luminescence appears to me to lie in the fact that in photoluminescence we have the only case, so far as I know, where the mode of excitation is definite and subject to control. Excitation by kathode rays probably comes next in order of simplicity. In a way it seems absurd to use the word simple in referring to either of these modes of excitation. But if we try to form a picture of the complex conditions that must exist in a flame, or arc, or spark, and compare such cases with the luminescence produced by monochromatic light or by kathode rays of constant and known velocity, it is like comparing the howling of a mob with the sound of a tuning fork. With sufficient patience we might find out how a piano is made by listening to the sounds produced by a crowd of unruly children pounding on the keys. But we would have infinitely better chance of success if we could press one key at a time and observe the result. In the study of photo-luminescence this can be done. In fact it is exactly what Wood *has* done.

In other words, in the case of photoluminescence we can control the excitation. We can determine relations between emission and absorption, and are in a position to tell which of these relations are real and which accidental. It is not merely that we have two methods of attacking the problem of the mechanism of emission and absorption, instead of one; it means a great deal more than that. We can observe the effects produced by the mechanism; or we can determine what agencies cause the mechanism to operate; but, what is more important still, we can correlate these observations and determine what effect is produced by a given stimulus.

The spectra of photoluminescence, complex as they often are, are the simplest spectra that are known. Even Balmer's series loses its appearance of simplicity if we compare it with the constant interval series of the uranyl salts. It may perhaps be urged that the high frequency X-ray spectra possess greater simplicity. Possibly this is true. But the evidence of the most recent work does not support such a view; for as the methods of observation are improved there is every indication that the structure of these spectra is far more complex than was at first suspected. A recent photograph published by Seeman showing a part of the high frequency spectrum of platinum might well be taken for the photograph of an arc spectrum. The history of ordinary spectroscopy seems to be repeating itself. Just as we thought until quite recently that an X-ray spectrum contained only the K and L lines, so there was a time when it was thought that the sodium spectrum consisted of the D line only.

The study of ordinary luminescence cannot, however, take the place of the study of high frequency spectra as a means of determining atomic structure. There is every reason for believing that the X-ray spectra come from the nucleus of the atom; while, as Stark has pointed out, there are strong reasons for thinking that luminescence spectra originate in the vibrations of the valency electrons. In the study of luminescence we attack the outer defenses of the atom; by the aid of the high frequency spectra we attack the citadel. Our problem will not be solved until both are won.

It is interesting to note, however, that in the high frequency spectra themselves we have phenomena that are highly suggestive of luminescence. The characteristic X-rays have sometimes been called "fluorescent X-rays," in recognition of an analogy that is by no means superficial. Characteristic secondary rays are produced only by X-rays of wave-length shorter than that of the secondary rays emitted. Here we have the analogue of Stokes' law. For wave-lengths just a little shorter than that of one of its own characteristic rays a substance shows abnormally great absorption. In other words there is an absorption band immediately adjacent to the emission band on the short wave side. We have here exactly the same relation between absorption and emission that holds in practically all cases of fluorescence. Using data kindly furnished by Dr. Duane I have plotted these absorption bands for several elements and have obtained curves that have the same form as those observed in such substances as eosin and resorufin with ordinary light. Except that the wave-length scale is a thousand times smaller, the phenomena of fluorescence certainly appear to be duplicated in the high frequency spectra in every detail. It would appear, therefore, that the arguments in favor of the study of luminescence spectra will apply equally well to the case of X-ray emission.

In this brief presentation I have not had time to refer to many important phases of my subject. For example, the connection between luminescence and chemical action produced by light; the relation between luminescence and the photo-electric effect; the use of fluorescent dyes as sensitizers for photographic plates; the development of an E.M.F. by the action of light on cells with fluorescent electrolytes; and many other topics whose study is of interest both as an end in itself and as a means of attacking the general problem. My chief object will have been attained if I succeed in arousing interest on the part of some of my hearers in a subject which, in my opinion, has not received the attention that it deserves.

THE LAW OF FALL OF A DROPLET THROUGH HYDROGEN.[1]

BY R. A. MILLIKAN, W. H. BARBER, AND G. ISHIDA.

THIS paper presents the results of experiments made by the oil drop method on the law of motion of a spherical drop through hydrogen. The constant A in the correction term to Stokes Law as developed by one of the authors is not found to have quite the same value in hydrogen as in air. This means that in different gases the coefficient of slip is not one and the same function of the mean free path as Kundt and Warburg supposed it to be, and this in turn means that Knudsen's conclusion that the molecules of a gas suffer "diffuse reflection" or "re-emission" from a surface upon which they impinge is not in general tenable. Up to $(l/a) = .4$ the law of motion of an oil droplet through hydrogen is found to be given by

$$X = 6\pi\eta av\left(1 + A\frac{l}{a}\right)^{-1},$$

in which A has the value .820 and l is determined from the Boltzmann formula $\eta = .350\,\rho\bar{c}l$. The same type of formula seems to hold generally up to $l/a =$ about .4, but A for air and oil is now found to be .845 while for air and shellac it is 1.06.

These differences are interpreted as due to differences in the law of rebound of different molecules from different sorts of surfaces.

UNIVERSITY OF CHICAGO.

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[1] Abstract of a paper presented at the Chicago Meeting of the Physical Society, November 28, 1914.

NOTES ON THE ATOMIC NUCLEI.[1]

BY WILLIAM DUANE.

THE work of Sir Ernest Rutherford and his students on the scattering of α-particles has added great interest to the hypothesis according to which an atom consists of a positively charged nucleus surrounded by negative electrons. The data obtained from experiments on the scattering determine upper limits for the radii of the nuclei (supposed spherical), the limit for gold being 3×10^{-12} cm.

In order to account for the α- and β-rays, which are supposed to come from the nuclei of the radio-active atoms, and also for the relations between the chemical properties of successive radio-active elements, we assume that in general a nucleus consists of positive and negative electrons with an excess of positive charges.

A difficulty arises here. How can a lot of positive electrons remain packed so closely together? They ought to fly apart under their mutual repulsive forces, for the electrostatic forces, varying as the inverse square of the distance, cannot hold them in stable equilibrium.

It is not necessary to go beyond the classical electro-dynamics to find forces of sufficient magnitude to overcome the electrostatic repulsions. A simple calculation will show that, if two nuclei have magnetic moments equal to that attributed to the iron atom, their magnetic attraction will overcome their electrostatic repulsion, provided that the distance between them is of nuclear magnitude.

Let us assume that two iron nuclei, each having the charge E and the magnetic moment M, are placed at the distance r apart, with unlike poles pointing toward each other. The electrostatic repulsion between them is E^2/r^2 and the magnetic attraction, $6M^2/r^4$, if r is large compared with their linear dimensions. The charge E on the iron nucleus equals $26 \times 4.77 \times 10^{-10}$. In calculating the magnetic moment M of the iron atom we may take the maximum value of the magnetization in iron obtained by B. O. Peirce,[2] namely 1796. Dividing this by the number of atoms in a cubic centimeter of iron, 8.612×10^{22}, we get $M = 2.086 \times 10^{-20}$. If r_0 is the value of r for which the electrostatic and magnetic forces are equal to each other,

$$\frac{E^2}{r_0^2} = \frac{6M^2}{r_0^4},$$

and putting in numerical values,

$$r_0 = 4{,}078 \times 10^{-12},$$

a quantity of nuclear magnitude, but somewhat greater than the radius of a gold nucleus.

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[1] Abstract of a paper presented at the New York Meeting of the Physical Society, February 27, 1915.

[2] Proc. of the American Academy of Arts and Sciences, June, 1913.

If the distance between the nuclei is less than r_0 they are held together, and if this distance exceeds r_0, they fly apart.

This suggests an interesting theory of the mechanism of α-radiation. Let us suppose that, owing to internal agitation, a portion of the nucleus of a radioactive atom gets thrown out by chance just beyond the point where the magnetic force can balance the electrostatic. This portion of the nucleus will then fly off just as an α-particle does.

We can estimate its final velocity as follows: Let E and E' be the charges on what is left of the nucleus and on the α-particle respectively, M and M' their magnetic moments and m and m' their masses respectively. If r_0 is the distance between them when the magnetic and electrostatic forces balance, and if the motion is along their common axis, the total work done after the particle passes this limit is

$$W = \int_{r_0}^{\infty}\left(\frac{EE'}{r^2} - \frac{6MM'}{r^4}\right)dr = \frac{EE'}{r_0} - \frac{2MM'}{r_0^3}.$$

For $r = r_0$, $EE'/r_0^2 = 6MM'/r_0^4$, and hence

$$W = \frac{2}{3}\frac{(EE')^{\frac{3}{2}}}{(6MM')^{\frac{1}{2}}}.$$

Since the kinetic energy divides itself between the two moving parts in the inverse ratio of their masses, we have for the final velocity v of the α-particle

$$v^2 = \frac{4}{3}\frac{(EE')^{\frac{3}{2}}}{(6MM')^{\frac{1}{2}}}\frac{m}{(m + m')m'}.$$

The question now arises: what values must be assigned to the magnetic moments? It is natural to suppose that the magnetic moments of the nuclei are due to the magnetic moments of the positive electrons composing them. If so, the maximum value the magnetic moment of a nucleus can have (namely when all the positive poles of the electrons are turned in the same direction), should be approximately proportional to the atomic weight of the atom, and we may calculate from this the minimum value that v can have. The smallest α-ray velocity known is that of the α-particle from Uranium I. The atomic number of this element being 92, we have $E = 90 \times 4.77 \times 10^{-10}$, $E' = 2 \times 4.77 \times 10^{-10}$, $m = 234 \times 1.662 \times 10^{-24}$, $m' = 4 \times 1.662 \times 10^{-24}$, and from the magnetic moment of the iron nucleus

$$M = \frac{2.086 \times 10^{-20} \times 234}{55.47}, \quad \text{and} \quad M' = \frac{2.086 \times 10^{-20} \times 4}{55.47}.$$

Putting these in the formula the minimum value of v becomes

$$v = 1.36 \times 10^9.$$

The most recent measurements of α-ray velocities are those of Sir Ernest Rutherford and Mr. Robinson,[1] who give for the velocity of the α-particle from Uranium I the value 1.37×10^9, in exceeding close agreement with the calculated minimum value.

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[1] Phil. Mag., Oct., 1914.

The other 19 α-ray velocities range up to 2.06×10^9. These can be explained by giving proper values to M supposing that a few of the electrons are reversed and perhaps by assuming that the α-particle is projected in some direction other than along the common magnetic axis, in which case the 6 in the formula becomes smaller.

Doubtless the problem is more complicated than this elementary calculation presupposes. Further a single fact does not prove a theory. On the other hand the fact that we can calculate from magnetic data α-rays velocities which differ from the results of measurement by less than the experimental errors, does appear to have a certain significance, especially when taken in connection with certain other facts, that I hope to present to the Society at some future time.

HARVARD UNIVERSITY.

X-RAYS PRODUCED BY SLOW-MOVING CATHODE RAYS.[1]

BY ELIZABETH R. LAIRD.

IN these experiments cathode rays from a Wehnelt cathode fall on an anticathode. The Röntgen rays so produced pass through a well shielded window into a measuring vessel, where their presence is indicated either by the charging of a metal plate in high vacuum, or by the ionization produced when the pressure there is a few millimeters. The window is covered with an airtight celluloid film. The variation in the intensity of the radiation as measured by the photo-electric effect is shown in the curve Fig. 1. The sensitiveness of the electrometer was 2.5×10^{-15} ampere per scale division per minute. An effect was not obtained with a primary P.D. less than 200 volts. The same was true when the sensitiveness was increased by the use of the ionization method, although at 550 volts the current was increased more than a hundred times. Experiments were made with other windows. Effects obtained when the window was not quite airtight were shown to be false, in one case light from the Schumann region falsified the results. Some measurements were made on the absorption of these different substances. The celluloid films used transmitted from 40 per cent. to 70 per cent. of the radiation. The absorption in them remained roughly the same when the primary potential was varied from 300 to 1,300 volts.

Aluminium, copper, platinum, and quartz used as anticathodes gave practically the same intensity of radiation, a smaller amount was obtained from the gas alone, *i. e.*, with the anticathode displaced.

Experiments were made to measure the velocity of the secondary electrons. The results would show that with a primary voltage of 550 some electrons are present with velocities corresponding to 100 volts or more. The difficulty of avoiding secondary effects from the walls or window of the chamber has not been entirely overcome, the correction for this would be expected to make the velocities higher.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 28–31, 1914.

Experiments were also made with another form of apparatus to test the polarization of the radiation. Only a slight amount of polarization was found.

The results with cathode ray velocities less than 200 volts do not agree with those of Dember and of Whiddington. The properties of the radiation as far as observed with the primary potential in the neighborhood of 550 volts are those of the Entladungsstrahlen from the spark at atmospheric pressure.

These experiments and the following ones were made while the writer was holder of the Sarah Berliner Research fellowship for women.

MT. HOLYOKE COLLEGE.

X-RAYS FROM THE ELECTRICAL DISCHARGE.[1]

BY ELIZABETH R. LAIRD.

IT has been found that the rays from the discharge in air at a pressure of 6 mm., previously known as Entladungsstrahlen at diminished pressure, cause a secondary radiation of electrons when falling on a metal plate in a high vacuum, and that the velocity of at least a portion of these electrons measured by an retarding field corresponds to 3,500 volts. The variation with pressure of the ionization produced between parallel plates leads also to the inference of a secondary radiation which is inappreciable after travelling a distance 0.017 cm. in air. The corresponding mass coefficient of absorption in aluminium was found to be approximately 590. These data are of the order of those obtained with X-rays of K type from calcium or L type from silver. These magnitudes show that one should not expect these more penetrating Entladungsstrahlen from a steady discharge at this pressure.

MT. HOLYOKE COLLEGE.

AN AGGLOMERATION THEORY OF THE VARIATION OF THE SPECIFIC HEAT OF SOLIDS WITH TEMPERATURE.[1]

BY ARTHUR H. COMPTON.

THIS work is based on the assumption that a degree of freedom of an atom in a solid cannot possess less than a certain critical amount of thermal energy. If its total energy falls below this value, the degree of freedom becomes "agglomerated," and remains in this condition until it again receives energy greater than the critical value.

The probability that a degree on freedom shall remain "unagglomerated" is found to be,

$$P = e^{-\epsilon/2RT} = e^{-\tau/T} \qquad (\tau = \epsilon/2R),$$

where ϵ is the assumed critical energy. The ratio of the specific heat at the relative temperature T/τ to its value at infinite temperature is then found to be,

$$C_v/C_\infty = e^{-\tau/T}(\tau/T + 1).$$

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, February 27, 1915.

This expression for the variation of the specific heat with temperature agrees very well with the experimental data, apparently better than the formulæ of Einstein and Debye which are based on the quantum hypothesis.

Princeton University.

A New Device for Rectifying High Tension Alternating Currents.[1]

By Saul Dushman.

THE action of the rectifier (kenotron) depends upon the emission of pure electron currents in extremely high vacua from an incandescent metal, when the latter is made cathode. Different types of kenotrons have been devised, such as a "headlight" tungsten filament placed inside a molybdenum cap, or a molybdenum cylinder with the tungsten filament placed along its axis. The current carrying capacity of the kenotron depends only upon the area and temperature of the filament (Richardson equation for electron emission), while the minimum voltage drop (V) depends upon the area, shape, and distance apart of the electrodes, and increases with the current actually rectified (i) according to an equation of the form

$$i = k \cdot V^{\frac{3}{2}}$$

(Langmuir's "space charge" equation). When i is measured in milliamperes, the magnitude of k varies in usual cases from 5×10^{-3}, for kenotrons suitable for 100,000 volts D.C. to 250×10^{-3} for kenotrons designed for 10,000 volts D.C.

Owing, however, to the fact that the filament temperature limits the maximum current which the kenotron can rectify, it is possible for the voltage over the latter to exceed the value given by the above equation, as the rectifier takes the difference between the maximum voltage available and that consumed in the load. Care should therefore be taken in using the kenotron to avoid short-circuits of the load, or some form of protective device should be used.

The actual energy losses in the kenotron may be reduced to less than two per cent. of the energy rectified.

Currents as high as 1,500 milliamperes may be rectified, but it is much more convenient to design the kenotrons so that each unit controls about 10 kw. As two or more kenotrons can be operated in parallel, this presents no limitation to their use. An arrangement of two or four kenotrons with a transformer and condensers will give direct current which can be made as free from pulsation as desired.

A detailed article dealing with this subject will be found in the General Electric Review for March, 1915.

Research Laboratory,
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Schenectady, N. Y.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, February 27, 1915.

THERMAL CAPACITY OF TUNGSTEN AT INCANDESCENT TEMPERATURES, AND AN APPARENT LAG OF RADIATION INTENSITY WITH RESPECT TO TEMPERATURE.[1]

BY A. G. WORTHING.

THE characteristic equation for a uniform filament mounted in an evacuated bulb, heating or cooling from one temperature to another due to a change in the heating current is

$$IV = f(T) + cm\frac{dT}{dt}$$

on the supposition that it passes through a succession of steady states. I, V and T represent the instantaneous values of current, potential drop, and temperature, m the mass of the filament, c the thermal capacity of the substance of the filament and t time. The three terms represent respectively the rate of heat production in the filament, the rate of radiation of energy from the filament, and the rate of change in the heat energy of the filament. The instantaneous values of I and V were measured on a potentiometer with the aid of a pendulum device. The values assumed for $f(T)$ were the wattages under steady current conditions corresponding to the resistances given by V and I. In some cases the cooling effects of the junctions were eliminated by taking the differences obtained using two filaments differing only in length when heated by the same current. In all cases it was found that the c–T relation obtained when the filament was heated from some low temperature to some higher temperature, was different from that obtained when it was cooled from the higher temperature to the initial low temperature. The difference was always consistent with the assumption that while the temperature is changing, the radiation intensity lags with respect to the temperature as determined by resistance measurements. Assuming the mean of such c–T relations to be the desired relation, and the temperature scale that determined by Mendenhall and Forsythe the following values have been obtained.

T in °K	c in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$
1,600	.042
1,800	.044
2,000	.047
2,200	.050

Results thus obtained are in good agreement with results obtained by a slight modification of Corbino's method in which the same filaments were used.

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CLEVELAND.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 27–28, 1914.

On the Reflecting Power of a Certain Selenium Crystal.[1]

By L. P. Sieg and F. C. Brown.

THE reflecting power, and other optical constants of metallic and amorphous selenium mirrors have been determined several times. The latest work has been done by Foersterling and Fréedericksz.[2] While working with large selenium crystals the question arose as to whether or not the optical properties of these crystals were the same as for the metallic modification or the amorphous varieties, or differed with the different types of crystals. Only a preliminary study was made, but work is being done in this laboratory toward obtaining a complete study of the optical properties. The reflecting power of the selenium as used by Foersterling and Fréedericksz was practically constant from wave-length 0.289 μ to 0.740 μ, varying from 0.36 to 0.25 at the longer wave-length. The present work indicated with certainty that the reflecting power for a lamellar crystal, from 0.37 μ to 0.80 μ was practically constant. Exactly what the coefficient is, has not been determined with any great accuracy, as the principal concern was to discover any variations, if any, in the reflecting power. This information was of great importance in connection with work on the light-sensibility curves.

State University of Iowa.

The Arc in a Longitudinal Magnetic Field.[1]

By R. F. Earhart.

SOME experiments were made with a carbon arc, using both cored and solid carbons, when the arc was placed in a uniform magnetic field. The lines of magnetic force were parallel to the axis of the carbon electrodes. The effect of establishing fields varying up to 2,000 c.g.s. units was to reduce the current and to increase the P.D. between the terminals. The behavior was studied by determining the characteristic curves for the arcs with fields of different strength. The characteristic curve produced when the field is established is similar to one which would be obtained by lengthening the arc. It was noticed that the heat developed at the positive carbon was increased when the field was established. In such case an increased length of carbon became red hot. This indicated that the anode fall in potential had been increased. Such was found to be the case when an exploring electrode was introduced. The cathode drop was increased but the anode drop had a greater relative increase than the cathode drop. The instability of the arc is increased with the application of the magnetic field. Unequal consumption of the carbon tips causes considerable difficulty.

Ohio State University.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 27–28, 1914.

[2] Ann. d. Phys., 43, p. 1227, 1914.

TRANSMISSION OF SOUND THROUGH FABRICS.[1]

BY F. R. WATSON.

THE transmitting power for sound of different materials was determined by allowing sound to pass through the material in question and noting how much the intensity was diminished as compared with the unhindered sound when the material was removed. A whistle blown by a constant air pressure and backed by a parabolic reflector directed the sound through an open doorway into an adjacent room where its intensity was measured by the deflection of a Rayleigh resonator. One, two and three layers of material were then placed successively over the doorway and the intensities measured each time. The preliminary results indicate that the intensity falls off in a decreasing geometrical progression as the thickness of material increases in an arithmetical progression.

UNIVERSITY OF ILLINOIS.

A DIFFERENTIAL DYNAMIC METHOD FOR THE ACCURATE DETERMINATION OF THE VAPOR PRESSURE LOWERING OF SOLUTIONS.[1]

BY E. W. WASHBURN.

THE chief sources of error in the determination of vapor pressure lowering of solutions by the gas-saturation method as heretofore carried out are (1) the difficulty in measuring with sufficient accuracy the large volume of gas aspirated; and (2) the error due to temperature variation in successive experiments. Both of these sources of error can be practically entirely eliminated by placing the saturation trains, containing the pure solvent and the solution respectively, close beside each other in a well stirred constant temperature bath and aspirating the gas through both saturation trains in succession, the solvent vapor being removed from the gas stream by suitable absorbers placed immediately after the last saturator in each train. Under these conditions it is not necessary to know the volume of the gas aspirated, which can, therefore, be made as large as desired. Moreover, temperature variations even as large as 0.1 degree in a well stirred bath will not produce an appreciable error since both solution and solvent are affected nearly alike.

With this method and with solution in the first saturator and pure solvent in the second the relative vapor pressure lowering is given by the following expression:

$$\frac{p_0 - p}{p_0} = \frac{D_m(B - P_1 - p_0) - m_0 D_p}{m_0(B - P_2) - D_m p_0}.$$

D_m is the difference in the amounts of solvent vapor taken up by the two absorbers respectively and this difference is directly determined by placing the

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 27–28, 1914.

absorbers (which are identical in form) on opposite pans of a balance. m_0 is the mass of solvent evaporated from the saturator containing the solvent, as determined by the increase in mass of the second absorber. B is the barometric pressure. p_0 is the (approximate) value of the vapor pressure of the pure solvent. P_2 is the difference between the barometric pressure and the pressure at which the aspirated gas leaves the second saturator while $D_p(= P_2 - P_1)$ is the difference in the pressures at which the aspirated gas leaves the two saturators respectively. Both P_2 and D_p which are very small are directly and accurately measured by means of two small inclined differential water manometers which are connected at the proper points in the system.

The precision of the result is wholly determined by the precision with which D_m is measured since all of the other quantities can be easily measured with 10 or 100 times the precision necessary. D_m increases with the concentration of the solution employed and with the quantity of air aspirated.

This method has been tested in this laboratory by Mr. H. B. Gordon and by Mr. E. O. Heuse. With molal aqueous solutions at 25° they find that an accuracy of about 0.25 per cent. is attainable in the value of $\frac{p_0 - p}{p_0}$ by this method.

Laboratory of Physical Chemistry,
University of Illinois.

NEW BOOKS.

Analytical Mechanics. By HAROUTUNE M. DADOURIAN. New York: D. Van Nostrand Company, 1913. Pp. xii+353.

This is a text-book of a grade intermediate between a part on mechanics in a college text-book on general physics and a treatise intended for graduate students. Apart from the numerous examples that are admirably worked out in the text, the excellent press-work, and the well-designed cuts, the most marked feature of the book (accentuated by the author) is the adoption of a modified form of Newton's third law of motion as the single fundamental feature in the treatment.

The author first quotes Newton's law in the form, "To every action there is an equal and opposite reaction, or the mutual actions of *two bodies* are always equal and oppositely directed," and then modifies the second clause to read, "or the sum of all the actions to which *a body* or a part of a body is subject at any instant vanishes," or $\Sigma A = 0$. The italics (ours) indicate the modification. It is arrived at by associating four concepts with the term "action" —force, torque, linear kinetic reaction, and angular kinetic reaction. These are introduced in succession as the development requires. Force, defined as "a vector the magnitude of which represents the action of one body on another" and torque, "the vector magnitude which represents the angular action of one body on another," suffice for statics. Linear kinetic reaction is described as the resistance which a body offers to a force which accelerates it. The mass of a body is then defined as "a constant scalar magnitude which equals the quotient of the magnitude of the kinetic reaction of the body by the magnitude of its acceleration" and the measure of kinetic reaction is then defined as $-mf$ (acceleration). (The logical order of the ideas in this process is not quite obvious.) Thus the general law becomes for a single body $\Sigma(A_l + A_a) = 0$. "Since the two types of action are independent of each other, the sum of each type must vanish." $\Sigma A_l = 0$ (linear), $\Sigma A_a = 0$ (angular). (But should they be represented as additive, being of different dimensions?) This system evidently leads to great simplicity in the formula for the fundamental principle. But the multiple-valued concept "action," in its protean adaptibility, seems likely to be a source of some vagueness in the mind of a student. "Kinetic reaction" is d'Alembert's "reversed effective force," conceived, however, as an entity, not as a convenient fiction, or it is the equivalent of the long banished "force of inertia." It does not seem to have the intuitional element desirable for use in a fundamental principle; this is probably the element that has given Newton's somewhat illogical arrangement of his laws of motion their persistent vitality. Will not a beginner be troubled by finding that in the case of two connected bodies there are are four actions, a force and a kinetic reaction for each? The author seems himself to have difficulties in finding the right word in referring to kinetic reaction. He cannot of course speak of it as being exerted on or by a body, but refers to it as something which "manifests itself," which a body "displays" or which "appears" when the body is accelerated. Students are likely to have still greater difficulties in this respect. Language and thought are inseparable, and ideas that are not readily clothed in words are indistinct. Others (*e. g.*, Love) have, in fact, used kinetic reaction as meaning $+ mf$. Mass, from its definition, will share in whatever haziness there is in kinetic reaction; likewise kinetic energy, defined by work done against kinetic reaction (two minus signs being required in the integration p. 187). The "normal kinetic reaction" of a particle revolving in a circle recalls "centrifugal force" when this was regarded as a force driving the body from the center. Yet the author's attempt at a new formulation of axioms is interesting. But, on the whole, while we may not be prepared to follow the suggestions of Tait and Kirchhoff and banish force, replacing it by a time rate of transference of momentum or a space rate of transference of energy, it seems doubtful whether the way out of the difficulties is to be found in the introduction of new variants of the force concept.

But the above criticism of one aspect of the book (on which, however, the author lays stress) does not apply to its many admirable features. The author has especially done well in treating under the head of Dynamics many problems which are usually discussed under Kinematics, thus emphasizing the physical aspect of the subject.

A. W. D.

The Theory of Heat Radiation. By Dr. Max Planck. Authorized translation from the 2d German Edition, by Dr. Morton Mazius. Philadelphia: P. Blakiston's Son and Co., 1914. Pp. ix+225. Price, $2.00.

As the translator remarks, most of those directly interested in this book can read it in the original. But the difficulties inherent in Planck's treatment are such that probably many of these will welcome the opportunity of studying the subject without having their attention at all diverted by linguistic troubles. There will also, let us hope, be many less directly interested readers who would never dip into the book at all if this translation had not removed one of the difficulties. The translation is entirely adequate as to clearness, and the translator has added two useful appendices, one dealing with Stirling's formula, and the other a bibliography of the more important papers, reports, etc., dealing with the quantum theory in its general aspects. Some of these references are accompanied with brief abstracts. It would be very valuable if this bibliography could be extended and the abstracts amplified in a future reprint.

C. E. M.

Tensoren und Dyaden im Dreidimensionalen Raum. Ein Lehrbuch von E. BUDDE. Braunschweig: Vieweg and Sohn, 1914. Pp. xii+248. Price, Mk. 6.

A knowledge of vector analysis becomes daily of more and more importance to the physicist. This is not a book on vector analysis, but on that part of it which has to do with the mutual relations of pairs of vectors such that the components of either are linear components of those of the other. According to the terminology here adapted, if the matrix of nine coefficients is symmetrical we have a tensor, if not a diatensor. The geometry of these various relations is very thoroughly explained, together with the applications to linear deformations, and the applications to the differential geometry of strains in general. It seems to the reviewer as if the physicist might get on with far less extended knowledge than this book presents, but there is no doubt that it is very well presented. A. G. W.

General Chemistry. Part I. Principles and Applications. By LYMAN C. NEWELL. Boston: D. C. Heath and Co., 1914. Pp. vi+174. Price $1.25.

This is one of the good books now available for those who wish to teach or to study chemistry in the high schools. In the preface the author states that the one point kept in mind during the preparation of the book was that "principles and applications must go hand in hand. Principles are the foundations upon which applications rest. To teach either one exclusively is hazardous, for when separated one is as barren as the other is superficial." It may be wondered if in high-school chemistry a greater use of the concept of the molar volume of gases than is made in the usual text-book might not be a valuable aid in teaching the subject. It might be possible too, to so develop the subject of atomic weights as to show the student that these weights may be obtained without the use of Dalton's atomic theory.

A feature of this book which should increase the interest of the students is that it contains a set of about twenty-five experiments on the subject of foods.

W. D. H.

The Sun. By R. A. SAMPSON. New York: G. P. Putnam's Sons, 1914. Pp. viii–141.

An unusually good example of popular scientific exposition. In a small space it treats practically all the phases of solar investigation. The treatment is sufficiently popular to make it interesting reading for any one of ordinary information, and yet its scrupulous accuracy should give it a place in the library of the scientific observer. The author has evidently used great care in giving due weight to the most recent investigations, so that it is probable that if the work of Grotrian and Runge on the "So-called Cyanogen Bands" had been published before the book was in print he would have made less positive his assertion (p. 125) that cyanogen has been found in the sun.

L. B. T.

Cours D'Electricite Theorique. By J. B. POMEY. Paris: Gauthier-Villars, 1914. Pp. viii–396. Price 13 fr.

This course of lectures given to the students of the "École Professionnelle Supérieure des Postes et Télégraphes" should be interesting reading for any teacher of theoretical electricity, because of its wide difference from the English and German treatments which are more familiar in America. It suggests that the preliminary training of the French technical students must be very different from that of the corresponding American students and the usefulness of the book in the hands of American students must therefore be limited. As an illustration of the difference, Green's Theorem is nowhere mentioned, its place being taken by a number of special theorems,—the Theorem of Vaschy, the Functional Equation of Robin, the Formula of Ostrogradski, etc. Under the last named we recognize what we customarily call Gauss' Theorem.

It is hard to understand why the sixty odd pages on vector notation should be postponed till Chap. IV., when the notation would have been as useful in the three preceding chapters as in the following four. This chapter adds another to the already numerous hybrids between the Hamiltonian and Continental vector notations.

L. B. T.

Scientific Papers. By J. Y. BUCHANAN. Vol. I. Cambridge, The University Press, 1913. Pp. xii+54.

This book is simply a collection of fifteen oceanographical papers reprinted exactly as they were originally published elsewhere. They deal with observations made on the Challenger expedition and also on the S.S. *Buccaneer*. They relate to the distribution of salt, of temperature, and of absorbed gases in the ocean, to the exploration of ocean shoals and ocean basins, and to general methods of attacking problems of this character.

R. A. M.

The Spectroscopy of the Extreme Ultra-Violet. By THEODORE LYMAN. New York, Longmans, Green and Co., 1914. Pp. v+135. Price $1.50 net.

The spectral limits were first set by the human vision. Next came the extension of heat rays toward the red end of the spectrum and of actinic rays toward the violet. In the violet the limit was set by the absorption of the apparatus; and, as Schumann showed, by the absorption of the gelatine of the photographic plates and the gases through which the light was compelled to pass.

Lyman has improved upon the Schumann's apparatus by employing a grating vacuum spectrograph. He also very cleverly introduced a double slit. Through one slit he could photograph to extreme ultra-violet. Through the other slit he could obtain known lines. With the two sets of lines in juxtaposition the wave-lengths of unknown lines could be accurately measured. By farther reducing absorption, Lyman has succeeded in doubling (when measured in wave frequency) the limits of the Schumann region. The opacity of oxygen for these short radiations is particularly noteworthy.

This book is a brief (too brief) account of the work which has been accomplished in the extreme ultra-violet, known as the Schumann region. We need now, more particularly, to increase our information upon that part of the spectrum between the Schumann region and the limits of the sun's spectra.

B. E. M.

Text Book on Wireless Telegraphy. By RUPERT STANLEY. New York, Longmans, Green and Co., 1914. Pp. xi+344. Price, $2.25 net.

This is a text-book rather than a treatise, being intended for actual class-room use. Having in mind the needs of those who intend to become wireless operators, but who have little knowledge of electrical matters, and also the needs of amateurs who are interested in wireless telegraphy but not familiar with the principles on which it is based, the author begins with several chapters on the general subject of electricity and magnetism. These are followed by a chapter on oscillatory discharges and another on electric waves. About one third of the book is taken up with such preliminary work, after which the methods and apparatus of practical wave telegraphy are discussed in a manner which, is, on the whole, extremely clear and satisfactory. The weakest point about the book is the inadequacy of the treatment of the fundamental properties of electric oscillations and waves. It is hard to see how the latter parts of the book can be really appreciated by one who depends for his knowledge of these fundamental topics upon the two short chapters which Professor Stanley devotes to them. For one who is well grounded in in the physics of electric waves and oscillations the book will be found extremely interesting and valuable.

E. M.

Second Series. *May, 1915* *Vol. V., No. 5.*

THE

PHYSICAL REVIEW.

THE INFRA-RED TRANSMISSION AND REFLECTION OF A NUMBER OF THE ANILINE DYES.

BY J. B. JOHNSON AND B. J. SPENCE.

IN taking up the study of the infra-red tranmission and reflection of the aniline dyes, there are at least two points open for consideration. First the problem of chemical arrangement and optical properties is by no means solved, but rather in its infancy and any new data which may be added to it, will be of service. For the visible spectrum a large amount of data has been obtained, and a number of interesting conclusions have been drawn from them. On the other hand, for the infra-red spectrum there exists a meagre amount of data in comparison to the amount available and anything like a rigorous test of the theory relating chemical arrangement or constitution with absorption has not been possible.

Unfortunately in studying the infra-red properties one is very much restricted in the study, owing to the great opacity of most of the organic substances to the long wave radiation, consequently leading to the use of very small angled prisms and thin films. Thin films and small angled prisms are in many instances impossible to produce and their use when produced is not at all certain, in the study of the infra-red spectrum.

A second point for consideration in the study of these dyes is their reflecting power. The aniline dyes show the property of surface color to a marked extent and it is possible that this property may exist for other wave lengths than those found in the visible spectrum. Associated with the phenomenon of surface color or residual rays, one finds a weak transmission of the wave lengths so reflected. In considering the subject of metallic reflection it must be borne in mind that not all absorption bands or better, bands of weak transmission, correspond to periods of powerful reflection. The so-called absorption bands are not absorption bands in the true sense, for according to the electro-magnetic theory of light at these wave-lengths the energy does not penetrate into the medium upon which it is incident and give rise to heat (true absorption) but owing to the periodic motion of the electrons set up by the incident vibrations,

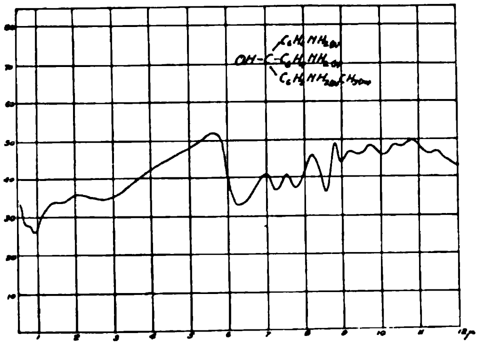

Fig. 1.
Rosaniline.

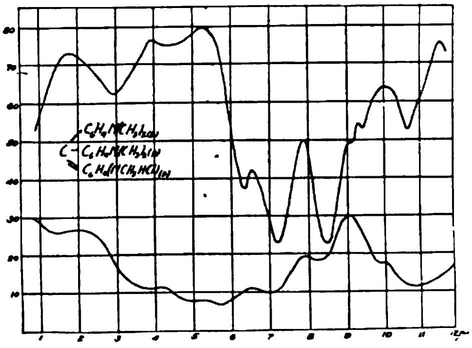

Fig. 2.
Methyl Violet.

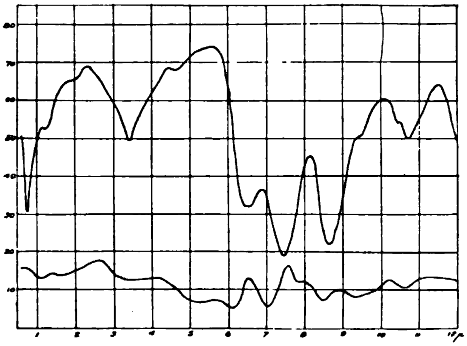

Fig. 3.
Paris Violet.

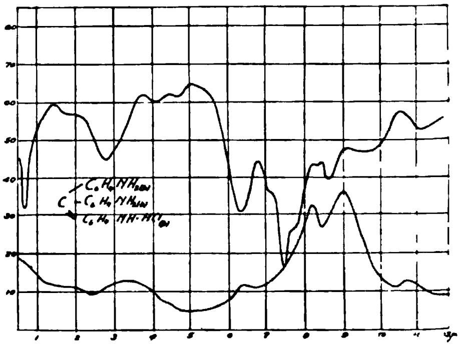

Fig. 4.
Fuchsine.

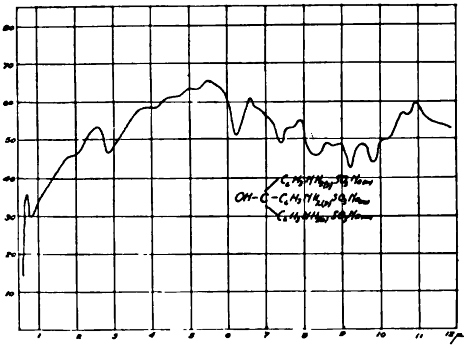

Fig. 5.
Ruby S.

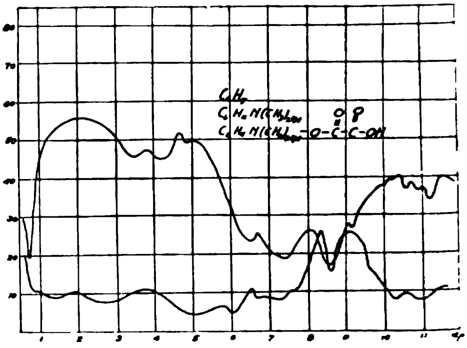

Fig. 6.
Malachite Green.

resulting in a neutralization of the electric intensity at the surface, the energy will be thrust back into the first medium as reflected energy.

A study of the dyes will not therefore be complete until an investigation of their refractive indices can be carried out for the infra-red region. Pfluger[1] has carried out an investigation of the refractive indices and absorption coefficients of the aniline dyes using very small angled prisms. The problem however dealing with the infra-red region is one of considerably more difficulty owing to the strong absorption of the dyes for the longer waves, and the lack of sufficient sensibility of the infra-red spectrometer.

Experimental Procedure.

The investigation was carried on by means of a specially built spectrometer[2] suitable for measurements in the infra-red region of the spectrum. The energy from a Nernst glower was focused upon the slit of the spectrometer by means of a concave mirror. The image of the slit was then brought to focus upon the thermo-pile after having been subjected to the procedure required by the Wadsworth mounting of the rock salt prism.[3]

The thermo-pile galvanometer combination was the same as that previously described by one of us.[4] The combination possessed a sensibility, such that the energy at the position of the sodium lines in the spectrum gave a deflection of 60 mm. with the galvanometer at a distance of a meter and a half from the galvanometer.

In order to determine the transmission of the dye a thin film of it in the solid state was drawn before the slit of the spectrometer by means of a suitable carriage, thus giving a reduced deflection for the desired wavelength. The ratio of the deflection to the deflection without the dye present gave the transmission of the dye for that particular wave length and thickness of the film.

For the determination of the reflection of the dye a modified procedure was necessary. The energy from the glower was focused upon the film of the dye and this image was in turn focused upon the slit of the spectrometer. The film was spread over a piece of glass and fastened to a sliding carriage which also held a piece of silvered mirror. The carriage was so arranged that the dye could be replaced by the polished silver surface. The ratio of the galvanometer deflection with the dye in position to the galvanometer deflection with the silver surface in place gave the percentage reflection.

The chief difficulty experienced in the work was the production of

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[1] Wied. Ann., *128*, 145, 1899.

[2] Astrophysical Journal, *39*, 243, 1914.

[3] Phil. Mag., 38, 1904.

[4] *Loc. cit.*

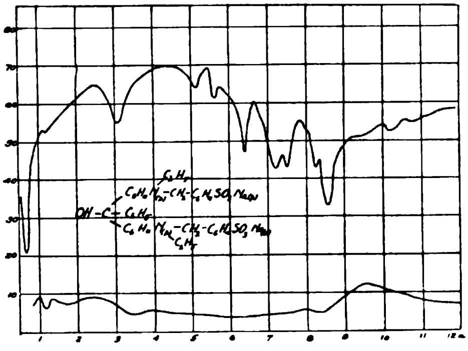

Fig. 7.
Guinea Green.

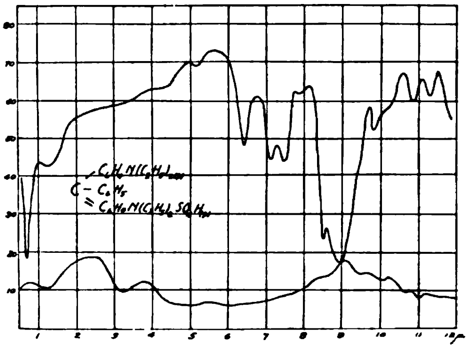

Fig. 8.
Brilliant Green.

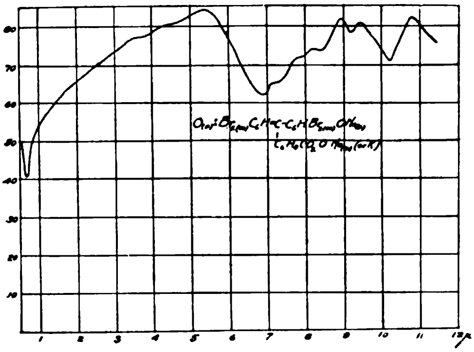

Fig. 9.
Eosine.

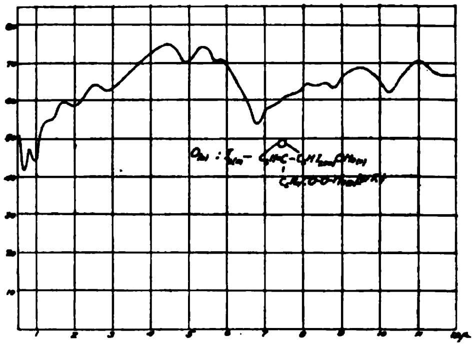

Fig. 10.
Bluish Eosine.

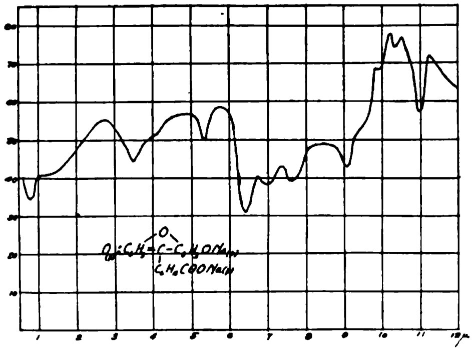

Fig. 11.
Uranine.

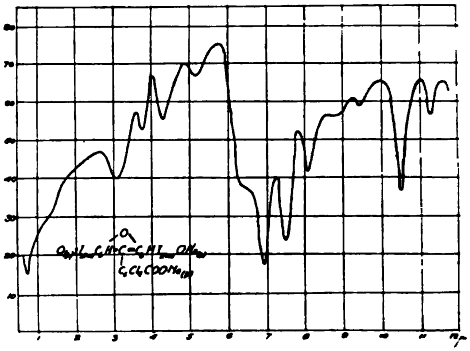

Fig. 12.
Rose Bengal.

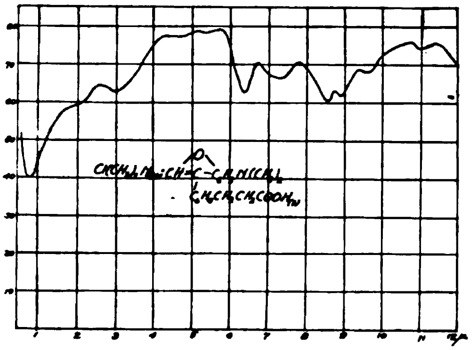

Fig. 13.
Acid Rhodamine.

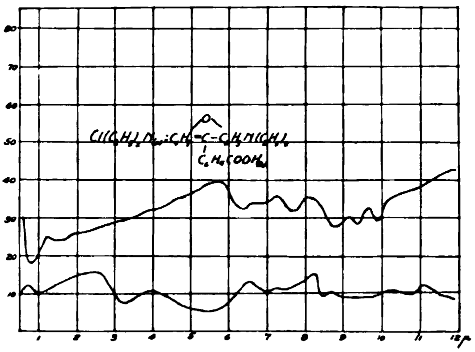

Fig. 14.
Rhodamine.

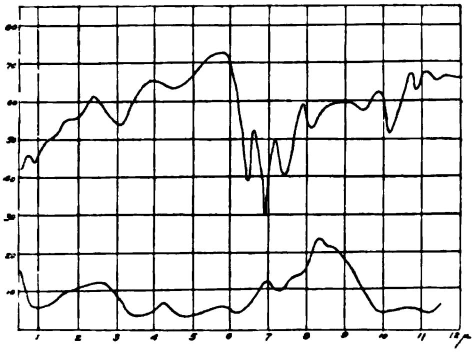

Fig. 15.
Erythrosin.

Fig. 16.
Chrysoidine.

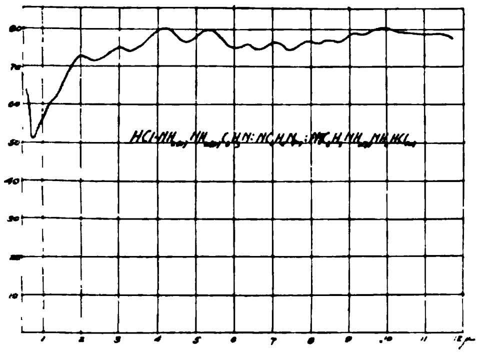

Fig. 17.
Bismarck Brown.

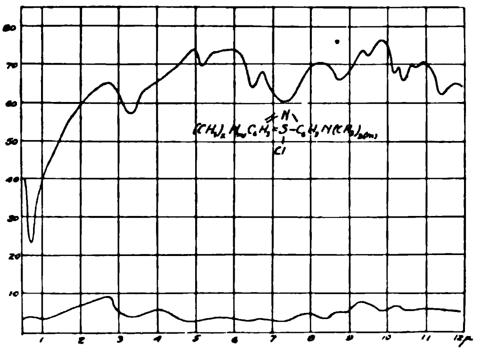

Fig. 18.
Methyl Blue.

suitable films from the dyes. The dyes were so opaque to the infra-red radiation that it was necessary to spread them over the surface of some diathermaneous medium, in this instance rock salt, in very thin films of thickness perhaps not more than a few wave lengths of visible radiation. The use of the rock salt made the production of the films very difficult, in as much as the only good solvent for the dyes is water. It seemed that no regular procedure could be used: each dye required its own particular treatment. In one or two instances a film was formed by melting the dye, but in most instances the films were obtained from solutions formed in amyl alcohol. Frequently, where solution was possible, films could not be obtained owing to the strong surface tension drawing the dyes up into small irregular patches on evaporation of the solvent. The production of films for reflection was in some instances more difficult, for a film which could be used for transmission was frequently too rough for reflection. Consequently it was impossible to obtain the reflection of all the dyes available. Many dyes which could have been used successfully were not available. It is hoped that the future may make these dyes available.

The chemical constitution of the materials was found in Remsen's Organic Chemistry, in Formanek's work and the greatest number in Greene's tables based upon the work of Drs. Shultz and Julius. The constitution of three of the dyes could not be found in the references and of cyanin and æsculin it is only known that they are a quinoline derivative and a glucoside respectively. The constitution of each substance accompanies its transmission curve.

The results are expressed in the form of transmission and reflection curves. The abscissæ are wave-lengths expressed in μ. The ordinates are per cent. transmission and reflection. Where two curves are plotted on the same coördinate system the lower of the two curves is the reflection curve.

The accuracy of the wave-length determination for the transmission curves is about .05 μ with the exception of the wide flat bands of very low transmission where the error is slightly greater. The error for the reflection curves is slightly greater than .05 μ, owing to the small amount of energy reflected corresponding frequently to not more than two or three millimeters galvanometer deflection.

Considering first the transmission curves with reference to the chemical constitution of the substances, a few points of interest are to be noted. There is a general similarity in all of the curves. All have one or two bands in the extreme red end of the visible spectrum causing in part the color of the substance. There is then a region comparatively free from absorption with a maximum of transmission in the region of the wave-

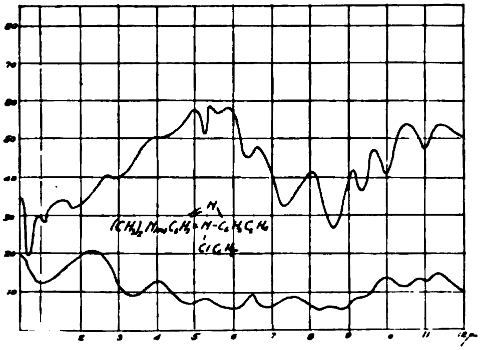

Fig. 19.
Neutral Blue.

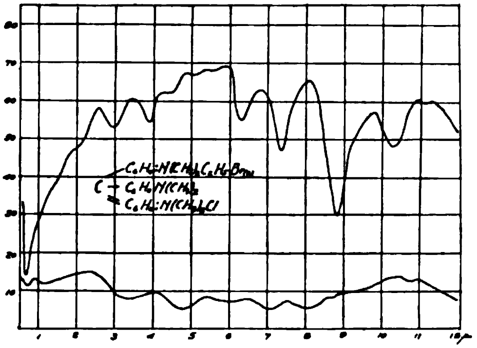

Fig. 20.
Methyl Green.

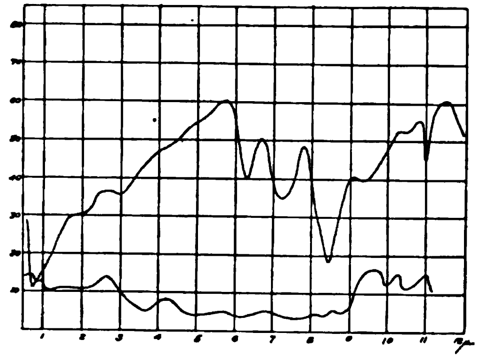

Fig. 21.
Cyanile Green.

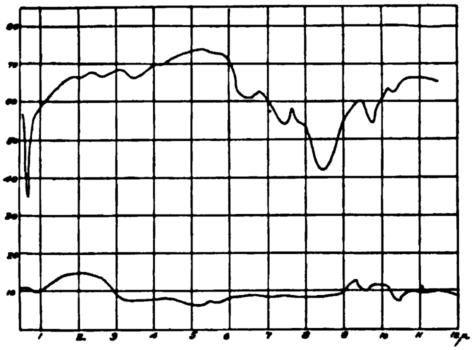

Fig. 22.
Neptune Green.

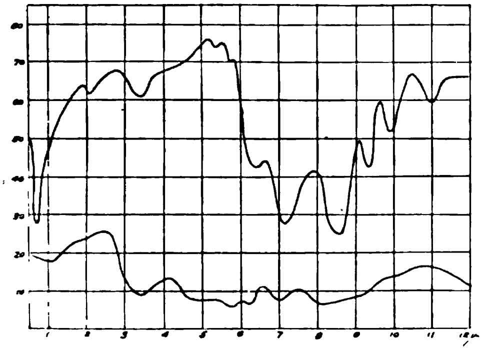

Fig. 23.
Steel Blue.

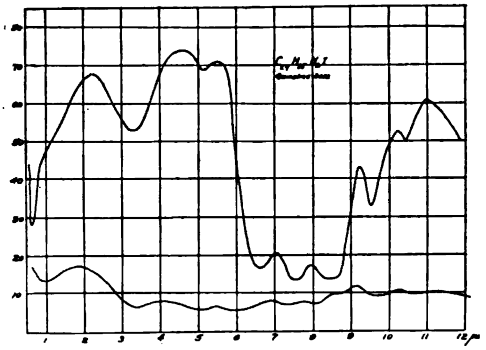

Fig. 24.
Cyanine.

length 5.5 μ. From this point on there is, in most cases, a sudden drop in transmission and then a region of complex absorption takes place to about the wave-length 9.0 μ, where the transmission again increases with or without bands.

In the region of complex absorption before 9.0 μ a higher dispersion would have revealed perhaps a large number of narrow deep bands. Further are to be noted the three deep bands in the interval between 6.0 μ and 9.0 μ of the triphenyl methanes and the triphenyl carbinols, and it would seem that the three substances of unknown composition, cyanile green, neptune green and steel blue, belong to these classes. The rosamine and quinoline substances show bands in this region but less accentuated. The substances named methyl violet and Paris violet are given as identical in composition as is also the case with eosine bluish and erythrosine. Their curves show differences in the disposition of the bands of minimum transmission. This may be due to impurities for it is very difficult to obtain dyes of guaranteed purity, or the differences shown may be in reality due to the differences in chemical arrangement which have not been noted chemically.

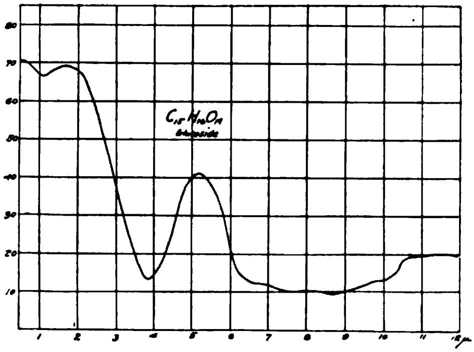

Fig. 25.

Aesculin.

Striking differences from the work of other observers appear in the transmission curves. Coblentz gives a list of bands assigned to different groups in the molecule as found by himself and others. The band at 3.42 μ ascribed by Julius to the CH_3 group occurs in but five of the curves, figs. 3, 6, 11, 17 and 24, two of which have the CH_3 group substituted in the amine group, two have no CH_3 groups and the fifth is unknown. The benzene ring is the next most prominent structural feature of these compounds but only two of the curves show a band at 3.25 μ, one has the 6.75 μ band and none the bands at 9.8 μ or 11.8 μ and but few the band at or near the wave-length 8.68 μ.

At least sixteen of the substances contain the OH or the NH_3 groups yet only five curves have the band at 2.95 μ, while none of them have the band at 6.1 μ. On the other hand, acid rhodamine is the only substance examined having the chlorine atom in the ring. It shows the band at 4.30 μ ascribed to chlorine.

From such conflicting data it is difficult to draw conclusions. The theory that certain chemical groups give rise to definite bands of minimum transmission certainly does not appear applicable to such complex substances. The large amount of evidence which seems to support the theory comes largely from a study of substances of fairly simple structure, but even with these substances the theory has a good many qualifications. With the more complex substances various constraints between the groups may well alter the position of the bands corresponding to them· However under these conditions it can not be said that to a certain chemical group there corresponds an absorption band at a definite wave-length.

Reflection.

The reflecting power of the dyes is generally small. The films from which the reflection was obtained were very thin. This should however make no difference in the reflection since the phenomenon sought is a surface one. There is however the possibility that the body color of the dye might make its appearance in the reflection curves but this would be fairly easy to detect for in general the body color obtained from the reflected light would correspond in position with the color shown on transmission.

A study of the reflection curves shows us that in a few instances there is comparatively strong reflection. It however is not of the intensity of metallic reflection. In some instances these maxima correspond to a minimum of transmission. Brilliant green shows a maximum of reflection corresponding to a weak transmission at the wave-length 9.0 μ. Erythrosine shows a maximum of reflection at 6.8 μ corresponding to a sharp minimum of transmission. A further increase of the reflecting power takes place beyond that wave-length corresponding to a rather complicated transmission from which it is difficult to draw definite conclusions. Paris violet shows strong reflection at 6.5 μ and 7.6 μ corresponding to weak transmission. Fuchsine shows a weak maximum of reflection at 6.4 μ corresponding to small transmission. Steel blue shows a broad reflection at the wave-length 8.5 μ corresponding to weak transmission at that point. It is also to be noted that erythrosin possesses a broad band of reflection at 9.4 μ corresponding to complicated transmission. Methyl violet possesses similar characteristics in the region of

10 μ. Likewise malachite green in the region of 9.5 μ. Whether any of the bands of reflection may be classed as residual rays seems rather doubtful, owing to the small value of the reflection coefficient. The method of multiple reflection would in all probability answer the question in the negative. There is one characteristic which nearly all of the dyes show on reflection. One notes on examining the curves that they reflect relatively well to the wave-length 2.8 μ where there occurs a sudden drop to a value of the reflection coefficient of a few per cent. The transmission curves are characterized by a weak transmission at the wave-length 3.0 μ rising to a maximum again rather suddenly. The reflection curves do not rise to a maximum immediately.

CONCLUSIONS.

The reflection and transmission of a number of aniline dyes have been obtained for the infra-red region of the spectrum to the wave-length 12 μ, thus adding more data to the problem of chemical constitution and absorption.

There is a similarity in the transmission curves for related compounds.

The theory that certain chemical groups in the molecule give rise to definite absorption does not hold with any degree of consistency for these complex substances.

The bands of maximum reflection in general coincide with periods of weak transmission. The evidence furnished does not seem to be conclusive in determining whether or not these are bands of metallic reflection. In all probability they are not.

UNIVERSITY OF NORTH DAKOTA,
November, 1914.

NOTE ON THE VALUE OF JOULE-THOMSON OBSERVATIONS FOR COMPUTING STEAM TABLES.

By Harvey N. Davis.

THIS note is offered for two reasons. In the first place, it is often supposed that Joule-Thomson or throttling experiments are of value chiefly in evaluating the thermodynamic or Kelvin scale of temperature, and in discussions of molecular attraction. As a matter of fact, such observations afford by far the best available means of determining for the use of engineers many of the important thermal properties of such vapors as steam and ammonia. In the case of steam, a point has now been reached where such observations are especially appropriate, since all but one of the remaining gaps can best be filled by this method. In the case of ammonia, much work has still to be done to supply the constants of integration that are necessary in this line of attack, but even here, Joule-Thomson observations will soon be necessary, if the most accurate results are desired.

And in the second place, it is believed that a compact resume of the underlying theory will be useful. In the course of this presentation, the essential identity of certain procedures that have often been regarded as distinct will be pointed out, and a variation of one of them suggested. Furthermore the form of proof presented, although obvious, seems not to have been published.

The fundamental data from which a set of steam tables can be most easily computed are: For the one-phase region, data on (1) the specific heat of superheated steam, and (2) the specific volume of superheated steam. For the two-phase region, data on (3) either the specific volume of saturated steam, or the total heat of saturated steam, or the heat of vaporization, (4) the specific heat of orthobaric water, (5) the specific volume of orthobaric water, and (6) the vapor pressure of wet steam.

Satisfactory data of the fifth and sixth sorts are already at hand. Satisfactory data of the fourth sort are sadly needed, but can hardly be supplied by anything resembling a Joule-Thomson experiment. But everything that is still needed under either of the first three heads, and the outstanding needs are numerous and important, can be supplied better by suitable Joule-Thomson experiments than in any other way.

In the first place, such experiments, if carried out with a heating coil, as suggested by Buckingham in 1903, can yield a direct determination of the specific heat of superheated steam. The heating coil is embedded in the plug of the ordinary experiment, and enables one to put a measured quantity of heat into each gram of steam as it goes through the plug. By this means what would ordinarily be a cooling can be reduced to zero, or changed to a warming of the emerging steam as compared with the entering steam. When the change of temperature is exactly zero, the whole apparatus can be kept at one temperature, and the heat losses of the ordinary sort are zero. It was this advantage that led to the proposal of the plan in the first place. Unfortunately there are heat losses of another sort in the isothermal experiment which, although not as large as in the adiabatic experiment, are more difficult to handle. Nevertheless, let us suppose that the heat losses of both sorts can be controlled, measured and allowed for, and that a series of experiments can be made at different rates of heat input, the high side pressure and temperature and the pressure drop being the same for all. Then if the heat supplied per gram of steam is plotted against the corrected change of temperature (Fig. 1), the result will be a straight line (if c_p is constant within the small temperature range in question) and the slope of this line will be c_p itself for the *low-side* pressure and temperature. To prove this one has only to notice that the plotted curve is really a curve of total heat against actual temperature for various conditions of the low side steam all at the same pressure. Its slope is therefore

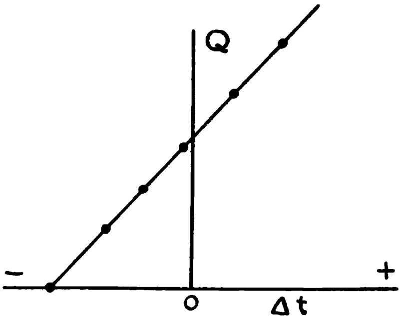

Fig. 1.

$$\left(\frac{\partial H}{\partial t}\right)_p = c_p.$$

Furthermore, since the t-intercept is obviously $\mu\Delta p$, the Q-intercept is $\mu c_p\Delta p$. Whether the inevitable heat losses of various kinds can be eliminated with sufficient accuracy to make this as good a method of measuring c_p as that of Knoblauch remains to be seen. At any rate, it will afford a useful check, either on c_p, or on the elimination of the heat losses, according to the relative accuracy of the previous knowledge of these two factors.

It should be noticed in passing that this is simply a combination in one experiment of the previously familiar principles of throttling experiments and of continuous flow calorimetry. The less the throttling provided for in designing the plug, the more does this method approach continuous flow calorimetry of the ordinary sort, like that of Knoblauch. But even in his case, where the throttling was made as small as possible, the correction for it is a troublesome one to apply unless it is handled from this point of view. And on the other hand, the introduction of as much throttling as is conveniently possible has the advantages both of helping to ensure that the steam is dry, and of providing twice as great a range of temperature for the specific heat measurements for the same maximum difference of temperature between the steam and its surroundings.

Besides this direct determination of c_p, Joule-Thomson experiments can give indirect but valuable information about c_p, in three substantially equivalent ways proposed originally by Dodge, by Davis and by Grindley. The value of each of these methods lies in the fact that it is easier, especially at high temperatures, to measure c_p at one atmosphere than at higher pressures; for each of these methods enables one to spread a c_p curve, determined at atmospheric pressure, into a family of curves covering as wide a range of pressures as are covered by the Joule-Thomson data. Dodge's and Davis's methods effect this by spreading c_p along lines of constant total heat or enthalpy; Grindley's spreads c_p along lines of constant temperature. The relative convenience of these three methods depends largely on how the Joule-Thomson experiments have been arranged and carried out.

Dodge's method requires that the experiments fall into groups, throughout each of which the high- and low-side pressures are held at fixed values: each group would contain experiments at different and well scattered temperatures. If such data are represented graphically by plotting high-side temperatures as abscissæ and low-side temperatures as ordinates, each group of experiments yields a curve which, at ordinary temperatures, lies below and close to the 45° line of symmetry of the figure, as in Fig. 2. Each point of this curve corresponds to a single experiment in which steam at a high-side temperature t, determined by the abscissa of the point, is throttled into steam at a low-side temperature t_0, determined by the ordinate of the point. Let the high- and low-side pressures corresponding to the whole curve be p and p_0. Then Dodge's theorem is that the slope of the curve at the given point is equal to the ratio of c_p at (p, t) to c_p at (p_0, t_0). If in each group of experiments, the low-side pressure is one atmosphere, the c_p curve at the high-side pressure is thus determined.

To prove this theorem, let Fig. 3 represent on the p, t plane two experiments corresponding to neighboring points of the curve. In one experiment steam is throttled from state (1) to state (2) with the total heat at the constant value H. In the second experiment steam is throttled from state (3) to state (4) with its total heat at the constant value $H + \Delta H$. At the constant pressure p (line 13), the average value of c_p would be

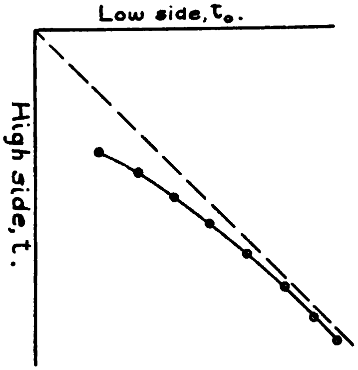

Fig. 2.

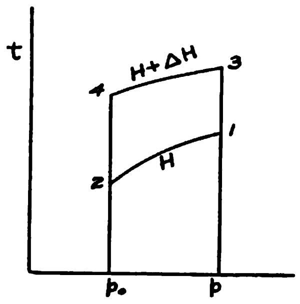

Fig. 3.

$$\bar{c}_p = \frac{\Delta H}{t_3 - t_1}.$$

At the constant pressure p_0 (line 24), the average value of c_p would be

$$\bar{c}_{p_0} = \frac{\Delta H}{t_4 - t_2}.$$

So

$$\frac{\bar{c}_p}{\bar{c}_{p_0}} = \frac{t_4 - t_2}{t_3 - t_1}.$$

But in Dodge's figure $(t_4 - t_2)$ would be the difference between the ordinates of neighboring points of the curve, and $(t_3 - t_1)$ would be the difference between their abscissæ. The ratio $\bar{c}_p/\bar{\ }_{p_0}$ is therefore equal to the slope of the secant. When ΔH approaches zero, this equation approaches the equation stated in words in Dodge's theorem.

This process is more accurate if modified by the use of the temperature difference $(t_0 - t)$ as ordinate instead of t_0 itself, as in Fig. 4. The curve then lies below and close to the t axis and can be plotted on a much larger scale. Its slope s for any value of t is now less by unity than before, and

$$\frac{c_p}{c_{p_0}} = 1 + s \quad \text{or} \quad s = \frac{c_p - c_{p_0}}{c_{p_0}} = \frac{\Delta c_p}{c_{p_0}}.$$

That is, the slope, which is now small, is the ratio of the increase in c_p between p_0 and p along a line of constant enthalpy to the value of c_p at the p_0 end of the interval. Since Δc_p is not more than a third of c_{p_0} for any pressure range occuring in ordinary practice, an accuracy of n per cent. in s would give an accuracy of $n/4$ per cent. in the computed c_p even under the most unfavorable circumstances, and a much higher accuracy over a large part of the plane. This offsets, at least in part, the disadvantage of having to use the derivative of an empirically determined function instead of the function itself.

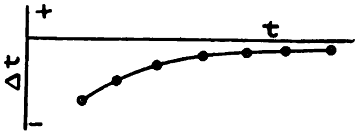

Fig. 4.

Davis's method is based on a differential equation that can be obtained directly from the modified form of Dodge's equation above. Let $p - p_0$ be called Δp_H. Then

$$\frac{1}{c_p}\left(\frac{\Delta c_p}{\Delta p}\right)_H = \frac{s}{\Delta p_H}.$$

s is the derivative with respect to t at constant p of the function $t_0 - t$, which is the drop of temperature through the plug and is negative. Let this function be called $-\Delta t_H$, so that a positive Δt may correspond to a rise of temperature as usual. Then

$$\frac{s}{\Delta p_H} = -\frac{1}{\Delta p_H}\frac{\partial}{\partial t_p}(\Delta t)_H = -\frac{\partial}{\partial t_p}\left(\frac{\Delta t}{\Delta p}\right)_H.$$

If now Δp_H approaches zero, this difference equation becomes

$$\frac{1}{c_p}\left(\frac{\partial c_p}{\partial p}\right)_H = -\left(\frac{\partial \mu}{\partial t}\right)_p,$$

where μ is the Joule-Thomson coefficient, and is the limit approached by $(\Delta t/\Delta p)_H$. This is Davis's differential equation.[1] Its integral is

$$c_p = c_{p_0} e^{-\int_{p_0}^{p}\left(\frac{\partial \mu}{\partial t}\right)_p dp},$$

the integration being at constant H. When μ is known as a function of

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[1] For other proofs of this equation see Davis, Proc. Am. Acad., 45, 1910, p. 291.

p and t, the integration can be effected by mechanical quadrature, and the ratio c_p/c_{p_0} determined. The chief advantage of Dodge's method over this is that, in Dodge's method, the integration is performed automatically by the steam itself for the pressure range covered by a set of experiments.

Grindley's method is based on a differential equation that can be deduced directly from this one. According to a familiar transformation formula,

$$\left(\frac{\partial c_p}{\partial p}\right)_H = \left(\frac{\partial c_p}{\partial p}\right)_t + \left(\frac{\partial c_p}{\partial t}\right)_p \left(\frac{\partial t}{\partial p}\right)_H = \left(\frac{\partial c_p}{\partial p}\right)_t + \mu\left(\frac{\partial c_p}{\partial t}\right)_p.$$

Therefore the last equation becomes

$$\left(\frac{\partial c_p}{\partial p}\right)_t = -\mu\left(\frac{\partial c_p}{\partial t}\right)_p - c_p\left(\frac{\partial \mu}{\partial t}\right)_p = -\left[\frac{\partial(\mu c_p)}{\partial t}\right]_p.$$

This is Grindley's equation. Its integral is

$$c_p - c_{p_0} = \Delta_t c_p = -\int_{p_0}^{p}\left[\frac{\partial(\mu c_p)}{\partial t}\right]_p dp.$$

this integration being at constant temperature.

This equation has certain advantages over that proposed by Davis. Thus it spreads c_p along lines of constant temperature instead of along lines of constant enthalpy, which is more convenient. It also determines the increment in c_p instead of a ratio, which is conducive to accuracy. And finally it involves the product μc_p instead of μ alone. Whether this is an advantage or a disadvantage depends on whether the isothermal or the adiabatic plug experiment can be carried out with greater accuracy.

It is at very high superheats that all three of these methods are most useful, because, under these circumstances, other methods of getting c_p are facing their greatest difficulties. Thus, while the experiments of Knoblauch determine the spacing of the c_p curves at different pressures with much accuracy at moderate temperatures, they fail entirely to separate these curves at and above 500° C., the experimental points at the various pressures being inextricably mixed. Even the roughest sort of knowledge of μ in this region would space the curves more satisfactorily, after the experiments had determined the average height at which they should lie.

Whether Grindley's or Davis's equation will prove to be more useful at high superheats will depend on whether μ or the product μc_p comes nearer to following a law of corresponding states. It has frequently been assumed that μ follows such a law.[1] If so, Davis's equation is the

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[1] For instance, by Buckingham, by Berthelot, by Callendar, and by Davis.

useful one. But μ is essentially a calorimetric quantity, and if it does follow a law of corresponding states, it is the only calorimetric quantity known to do so. The product μc_p on the other hand is a specific volume, and it was for specific volumes that the law of corresponding states was originally proposed. One would therefore have predicted *a priori* that the product μc_p would be more amenable to such treatment than μ. If so, Grindley's equation is the useful one.

Turning now to the specific volume of superheated steam, we have the well known relation

$$\frac{v}{T} = \frac{v_0}{T_0} + \int_{T_0}^{T} \frac{\mu c_p}{T^2} dT,$$

where the integration is to be carried out at constant pressure. For a perfect gas, μ would be zero, the integral would vanish, and v would be proportional to T at constant pressure. For steam, the integral appears as a small correction term on the ratio v/T. v can therefore be computed as a function of T along an isopiestic, if its value is known at any one point of the isopiestic. Fortunately v is known close to the saturation line from computations with the Clapyron equation, and from the experiments of Knoblauch, Linde and Klebe. This gives a starting point for every isopiestic between 1 and 10 atmospheres. Within this pressure range, the best way to get specific volumes at any temperature however high is undoubtedly to make measurements, not on v itself, but on the product μc_p.

This procedure has certain great advantages. In particular, the object of the experiments is to determine, not the whole quantity sought, but a relatively small correction term. For example, in computing the specific volume of steam at 50 lbs. per sq. in. abs. and 600° F. superheat, the whole correction term is probably not more than 5 per cent. of the answer sought. If, therefore, the correction term is known within 2 per cent. of itself, the specific volume is known within 0.1 per cent. of itself, which is as good as the accuracy of the initial volume used as the constant of integration. Furthermore, the correction term is not an observed quantity but the integral of an observed quantity. The only chance for a 2 per cent. error in the integral is a *systematic* error in μc_p amounting to 2 per cent. throughout the whole range. The allowable *accidental* errors in μc_p might be considerably greater than 2 per cent. for an accuracy of 0.1 per cent. in v.

Let us now turn to saturated and wet steam. It is almost certain that suitable Joule-Thomson experiments with superheated steam can be made to yield a more accurate determination of the *shape* of the *HT* curve of saturated steam than can be obtained in any other way.[1]

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[1] See Davis, Proc. Am. Acad., 45, 272, 1910.

Briefly, the fundamental principle is that if, by means of throttling experiments, we can plot the lines of constant H on the superheated steam plane, and if, by means of c_p values, for any one pressure, we can determine the differences ΔH from each curve to the next, we have a determination of the increase in H along the saturation line for each interval between points of intersection with our curves. If H is known by direct measurement at any one point of the saturation line, this process will give its value all along the line. Fortunately there are a number of good determinations of H between 0° C. and 160° C., particularly near 100° C. A good set of Joule-Thomson experiments is therefore all that is needed to determine a satisfactory HT curve over a considerable range.

This process, like that for computing the v of superheated steam, has the great advantage of concentrating the efforts of the experimenter, not on the whole quantity sought, but on a comparatively small increment term. Thus if H_{100} is assumed to be known, the term to be determined experimentally is never greater than 5 per cent. of H itself, and 1 per cent. on the correction term gives 0.05 per cent. on H, which is somewhat better than the accuracy of our present knowledge of H at the boiling point.

When the H curve is thus determined, it will be easy to compute the specific volume of saturated steam by means of the Clapyron equation, if only the specific heat of water and the vapor pressure curve are known. The latter is now well known over the whole range from 0° C. to the critical point, but our knowledge of the specific heat of water is very meager at high temperatures and very chaotic at ordinary temperatures.

Finally, when all these things have been computed, either from the satisfactory data already in hand or from a good set of Joule-Thomson data, an interesting check on the self-consistency of the whole steam table is afforded by Planck's equation

$$c_p = \frac{dH_{\text{sat}}}{dt} - \frac{L}{T} + T\left(\frac{dp}{dt}\right)\left[\left(\frac{\partial v}{\partial t}\right)_{p_{\text{steam}}} - \left(\frac{\partial v}{\partial t}\right)_{p_{\text{liquid}}}\right],$$

where L is the latent heat at the temperature in question. The derivatives in the last term refer to superheated steam and water close to, but not inside, the steam dome. The c_p thus computed is the limiting value on the saturation line approached by the c_p of superheated steam. The fundamental data from which the right hand side can be computed are (1) the value of $(dp/dt)_{\text{sat}}$, which is well known, (2) the value of L or H at 100° C., which is fairly well known, (3) a knowledge of the variations of L and H with temperature, which should depend chiefly on Joule-Thomson data, and (4) the value of $(\partial v/\partial t)_p$ for steam, which also should depend chiefly on Joule-Thomson data. The derivative for water is practically negligible. It is true that a knowledge of c_p itself, which is the quantity sought, is involved in the computation of the variation of L or H with temperature, but it happens that this indirect dependence of the right hand side on c_p is such as to make the computation insensitive to errors in the values of c_p originally assumed. The equation therefore affords a valuable method of successive approximations for computing c_p along the saturation line, where direct measurements are most difficult, as well as a useful check on the c_p curves in general.

It appears, then, that the only experiments that are now greatly needed to put our steam tables on a thoroughly satisfactory basis are a complete and accurate series of Joule-Thomson or throttling experiments, and a thoroughly satisfactory series of experiments on the specific heat of water, especially at high temperatures. Both sorts of experiments are now in progress in the Jefferson Physical Laboratory, and, I believe, elsewhere as well, and it is hoped that the results will be sufficient to serve the purposes which have been indicated.

Jefferson Physical Laboratory,
Cambridge, Mass., Jan., 1915.

THE RESULT OF PLOTTING THE SEPARATION OF HOMOLOGOUS PAIRS AGAINST ATOMIC NUMBERS INSTEAD OF ATOMIC WEIGHTS.

BY HERBERT E. IVES AND OTTO STUHLMANN, JR.

THE relationship between the characteristic spectra of the chemical elements and their atomic weights and chemical properties has been the subject of considerable study. Ramage,[1] Runge and Precht,[2] Watts[3] and Rudorf[4] may be mentioned among those who have sought for and established more or less definite connections between the frequencies of spectrum lines and atomic weights. In every case however there have been exceptions and discrepancies of such character as to indicate that while there is undoubtedly a real connection the true relationship has not been found.

Perhaps the most interesting contribution to this problem was furnished by Runge and Precht, in their attempt to determine the atomic weight of radium from spectroscopic evidence. They stated the following law: "In each group of chemically related elements the atomic weight varies as some power of the distance apart of the two lines of a pair," so that "the logarithms of the atomic weights and those of the distances when plotted as coördinates lie on a straight line for a chemically related group of elements." They are careful to apply this law only to "homologous" pairs of lines; homologous lines being characterized by similar behavior in the magnetic field.

Having established the generality of this law Runge and Precht applied it to the group of elements, magnesium, calcium, strontium, barium, radium. Extrapolating for the latter element they obtained a value of 257.8, which disagreed by 13 per cent. from the value obtained by Mme. Curie by chemical methods. Runge and Precht point out that the Curie value may be expected to be too low by reason of the effect of impurities. Nevertheless the high value obtained by them is generally considered incompatible with the place of radium in the periodic system and the spectroscopic method is to some extent discredited.

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[1] Proc. Royal Society, LXX., p. 3, 1901.

[2] Phil. Mag. (5), 476, 1903.

[3] Phil. Mag., July 1903, August, 1904.

[4] Zeits. Phys. Chemie, 50, p. 100, 1904.

The spectroscopic value would probably be entitled to more consideration were it not for the fact that other exceptions than radium were found to the law. The existence of exceptions of course detracts seriously from the applicability of any rule for purposes of prophesy. Thus boron and potassium were noted by Runge and Precht. With regard to boron they remark that it had not been examined in a magnetic field so that their choice of lines might be at fault. In regard to potassium the following highly significant remark is made: "It appears to us interesting that the straight line law is appreciably departed from precisely in the case of the element whose atomic weight in the periodic system points to an unknown disturbing cause, which produces the inversion of the positions of argon and potassium."

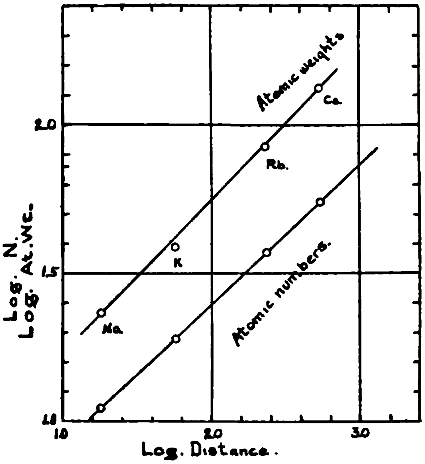

Fig. 1.

Within the past year it has been strikingly demonstrated by the work of Mosely[1] that the most characteristic figure connected with a chemical element is not its atomic weight, but its *atomic number*, which is identified with the charge on the positive nucleus of the Rutherford atom. Not only are these atomic numbers whole numbers but the various elements follow each other in the order of their chemical properties without the inversions found in the cases of nickel and cobalt, argon and potassium, tellurium and iodine, when atomic weights are considered. The periodic system should apparently be built around atomic numbers, not atomic weights.

It occurred to us that the problem of the relation between chemical properties and spectroscopic phenomena might be assisted by recourse

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[1] Phil. Mag., 27, p. 703, 1914.

to the newer reference frame. We have therefore re-plotted the figures used by Runge and Precht, with interesting results.

In Fig. 1 we have plotted the series sodium, potassium, rubidium, cæsium, both in terms of atomic weights and atomic numbers. It is at once clear that the "unknown disturbing cause" is the use of the non-significant atomic weight, for on the atomic number plot potassium is no longer an exception to the straight-line relationship.

In Fig. 2 is shown the series in which boron occurs. It too falls in line.

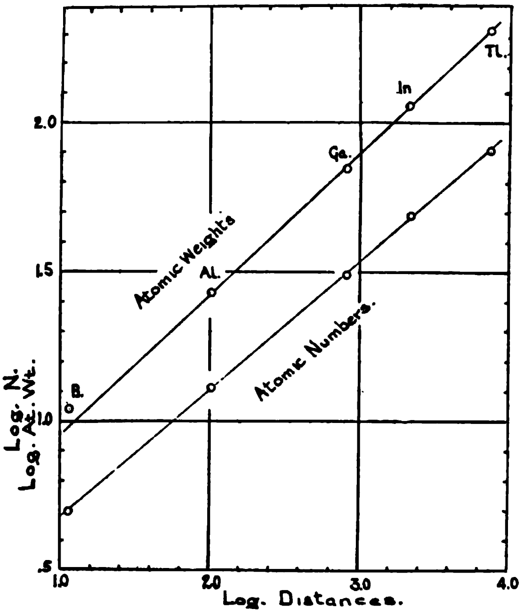

Fig. 2.

The data of these two figures were taken from the paper by Runge and Precht, and apply to lines which fulfill their criterion as to homologous character. Another exception to the law is pointed out by Rudorf, in the series zinc, cadmium, mercury. Upon plotting his data,[1] as we have done in Fig. 3, it appears probable that the reason for this exception is again the choice of atomic weights instead of atomic numbers, for the atomic number points fall on a straight line.

What happens when we attempt to obtain the atomic number of radium by this revised law? Fig. 4 shows the series from magnesium to radium, using again the data of Runge and Precht. Calcium, barium and strontium fall on a straight line, but magnesium falls slightly off. (The atomic number 13 would fit the case better than the number 12

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[1] Rudolf, loc. cit., p. 101.

which has been ascribed to this element.) Continuing the line through the calcium, barium, strontium group we obtain for radium the number 96. The atomic number ascribed to radium is actually 88.

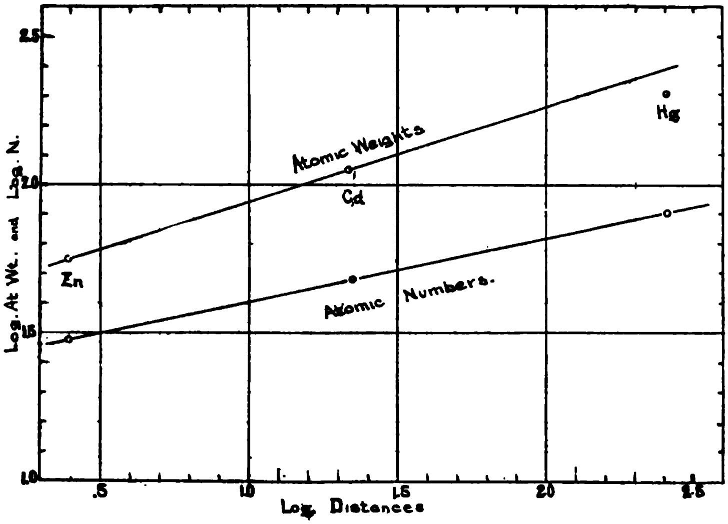

Fig. 3.

It appears, therefore, that while the exceptions which previously cast doubt on this relationship have been eliminated by the new method of plotting, the best it can do for radium is to reduce the discrepancy from 13 to 8 per cent., at the same time getting into trouble with magnesium.

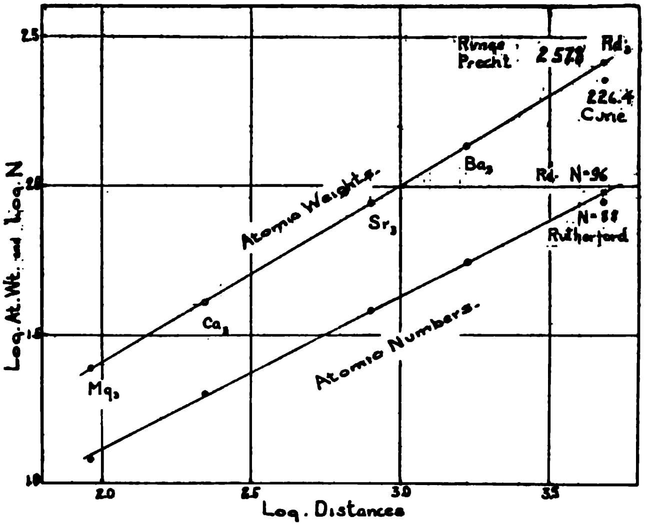

Fig. 4.

Against this, however, may be set the fact that the atomic number of radium has been derived only indirectly through its relationship to lead, and that of magnesium has not been experimentally determined. At any rate the relationship between line separation and atomic number is so very satisfactory in the case of the other groups of elements as to suggest the desirability of going over anew the experimental work on which the data depend in the magnesium-radium group.

It is of course obvious that this entirely empirical relationship must be, if true, a necessary consequence of the complete mathematical description of the structure of the atom. The fact that it is apparently a function of atomic numbers, on which the most recent picture of the atom is built, gives, we believe, some slight additional support to the idea of the nucleus atom. At the same time it suggests that a review of outstanding difficulties both in the periodic system and in series relations in spectra, might be undertaken with atomic numbers as a basis, with profitable results.

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PHILADELPHIA, PA., January, 1915.

THE CHANGE IN THE ELASTICITY OF A MILD STEEL WIRE WITH CURRENT AND EXTERNAL HEATING.

By H. L. Dodge.

THE effect of current and external heating upon the Young's modulus of a copper wire was described in a previous number of the Physical Review.[1] The present paper deals with a similar investigation of a mild steel wire, the more marked changes being an increased temperature range, namely 20° C. to 475° C., and slightly greater accuracy. For a detailed description of the apparatus and method of making the determinations the former paper should be consulted.

Improvements in Apparatus and Method.

Mention cannot however be omitted of certain changes which have resulted in greater accuracy. Attention was called in the previous paper to the desirability of having the specimen of wire free from mechanical interference between the two points of suspension. The only interference in the case of copper wire was the three thermo-couples of fine wire which did not seem to cause any inaccuracy in the results. Some changes in the method of measuring the temperature have made these unnecessary and in the present apparatus the specimen of wire hangs absolutely free.

As before, the temperature of the wire is determined by its change in length with increase of temperature. In the former paper the justification and advantages of this method were explained. The same statements apply in the present instance as the only changes have been in the process of finding the relation between temperature and length. This was found as follows:

A thermo-couple was carefully calibrated by means of a thermometer. It was then attached to the wire at the middle point and the relation between the temperature of this point and the length determined. As all the points of the wire were not at the same temperature it was necessary to find the relation between the average temperature and the temperature of the middle point. The heating box was maintained at a constant temperature of about 350° C. and a large number of thermocouple readings taken at various points on the wire. This not only

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[1] Phys. Rev., N. S., Vol. 2, 431, 1913.

established the relation between the average temperature of the wire and its length but also gave complete information concerning the temperature distribution. Under the above conditions the maximum variation of the temperature along the wire was about 40° C. while the error in the measurement of the average temperature was probably not more than 10° C. At lower temperatures the accuracy is of course greater, the error amounting to but one or two degrees at or near room temperature and perhaps five degrees at 150° C. At higher temperatures the possibility of error is of course greater amounting to about 20° C. at 475° C. The curve representing the relation between change of length and temperature was plotted and found to be a straight line within the limits of accuracy of the temperature measurements. The increase in length between 20° C. and 475° C., corrected for the stretch caused by the decrease in the modulus, was 3.67 mm. As the wire was 57.6 cm. between points of observation the mean temperature coefficient of expansion proves to be .000014 with a possible error of five per cent.

Considerably increased accuracy has been secured in the measurement of the stretch and consequently the modulus with the present apparatus by the use of new microscopes and micrometer slides with screws accurate to .001 mm.

THE SPECIMEN.

The sample of wire upon which the tests were made was obtained from the Driver-Harris Wire Co., Harrison, N. J. A chemical analysis of the wire secured from Mr. J. W. Whitfield of the firm of Booth, Garrett and Blair, Philadelphia, Pa., was as follows: Silicon, 0.057 per cent.; sulphur, 0.059 per cent.; phosphorus, 0.105 per cent.; manganese, 0.735 per cent.; carbon, 0.162 per cent.; iron (by differences), 98.882 per cent. The sample was pronounced a " mild " or low carbon steel.

The mean coefficient of expansion between 20° C. and 475° C. is 14×10^{-6} per degree Centigrade to an accuracy of about five per cent. The wire is .82 mm. in diameter. The portion between the points of observation was 57.6 cm. long. A weight of 2,109 grams was kept upon the wire continually, the modulus being determined by measuring the elongation produced by an additional weight of 2,252 grams. Certain additional facts regarding the loading, current, number of readings, time between readings, duration of tests, etc., appear in Table I. which contains the complete data of a characteristic series of observations with current heating. The other series differ materially only in method of heating or temperature range.

NATURE OF THE TESTS.

The preliminary observations made while the wire was being straightened and brought to a cyclic state revealed striking irregularities in its behavior. At first increase of temperature increased the modulus but this effect soon disappeared. Continued heating and testing gradually increased the modulus. This was probably due largely to stretching and straightening. Both current and external heating were employed and no effect characteristic of the method of heating could be detected. After a number of cycles of heating and cooling accompanied by stretching, the wire was brought to a cyclic state and the more extended tests made.

The first group of observations were with a temperature range of 20° C. to 300° C. The tests were with both external and internal heating and increasing and decreasing temperature and were so arranged as to reveal if possible any effects peculiar to the method of heating or the thermal route by which any temperature was reached. Later the temperature range was extended to 450° C. and to 475° C. and similar series of tests made. A few characteristic results are shown in Figs. 1, 2 and 3, explanations of which follow.

EXPLANATIONS OF THE CURVES.

Figs. 1, 2 and 3 represent graphically certain of the results that have been obtained. Table I. contains the complete data for series 19, Fig. 2. The data for the other curves do not differ materially in general character. In every case the dotted points represent determinations of the modulus with increasing temperature and the crosses those with decreasing temperature. Nearly all the points are the result of ten or more observations. When the terms " external " and " internal " heating are employed the former indicates that the wire was heated by means of a heating element of nichrome wire extending along the bottom of the enclosing box, while the latter term refers to heating by means of an electric current passing through the specimen itself.

In all of the statements regarding the absence of certain effects it should be understood that this refers to effects amounting to one per cent. or more. The present apparatus cannot detect variations in the modulus of a less amount. The accuracy of the work can best be judged from the curves. A change in the modulus of as much as ten per cent. corresponds to a difference in stretch of only 0.013 mm.

The first four series covered a temperature range of 20° C. to 300° C. with both external and internal heating and showed a practically linear relation between Young's modulus and temperature. Series 5, Fig. 1, was with external heating, increasing and decreasing temperature. Series 6 and 8 are plotted together. They were with internal heating, increasing and decreasing temperature. The results of the first eight series show that for temperatures below 300° C. the elasticity is a definite function of temperature, independent of manner of heating and free from any hysteresis effects.

It was next thought desirable to extend the temperature range by a considerable amount and to repeat the tests in various orders to ascertain whether the same relations hold for a greater range of temperature. Upon heating above 300° C. a very rapid decrease of the modulus was discovered, the rate of decrease becoming very marked at about 450° C. The results are shown in Fig. 1, series 9. At this temperature the wire stretched about one fourth of a millimeter, approximately .05 per cent. of its length. When the elastic limit is exceeded there should be an increase of the modulus for all temperatures. The next observation at room temperature showed an increase from 18.5 to 19.2 or 2.6 per cent. The increase of the modulus for other temperatures as well can be seen from Fig. 2.

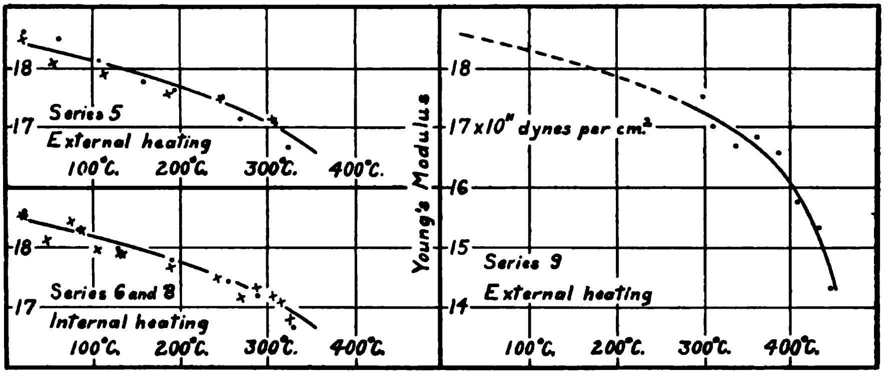

Fig. 1.

Change of Young's modulus of a mild steel wire with temperature.

The first three series of observations of Fig. 2 give the temperature variation of Young's modulus with external heating. Series 11 shows the type of curve, and the return of the modulus to the same value after a day of heating and stretching. Series 12 was taken under similar conditions. By yielding the same results it proves the total disappearance of all history effects except the very gradual increase of the modulus with continued heating and stretching. As the observations for decreasing temperature in the last two series were few, series 13 was made in order to learn whether the curve with decreasing temperature is the same as with increasing temperature. The results indicate the absence of any hysteresis effect. In order that the various series in this and the other figures may be more easily compared the curve which appears was drawn to fit a composite of them all. Its shape is exactly the same in every case the only difference being that it is gradually raised to correspond to the general increase of the modulus as the work progressed.

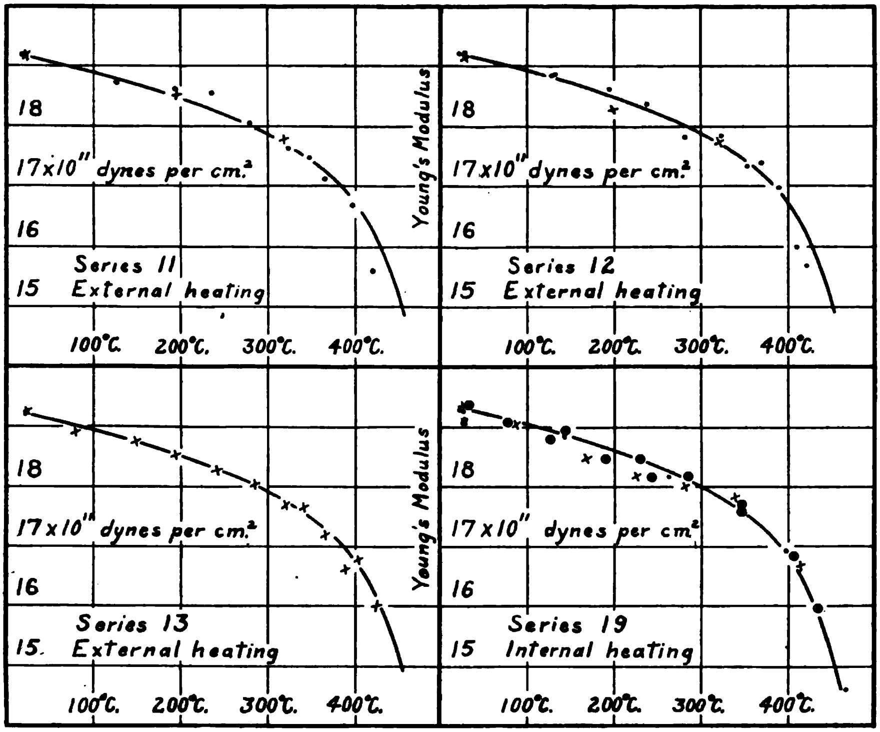

Fig. 2.

Change of Young's modulus of a mild steel wire with increasing and decreasing temperature and with internal and external heating.

All of the observations so far had been made with the wire enclosed in an asbestos board heating box so that the currents used in the wire and the heating element might be as low as possible. Walker[1] has found a great difference between the effects of internal and external heating, dependent in part upon the current density. He interprets these results as caused by the magnetic effect of the current, the maximum field which he secures having an average value of 31 gausses.

When series 19 (see Table I.) was taken an attempt was made to find this effect in case it were associated with residual magnetism. Between

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[1] Proc. Roy. Soc. Edin., Vol. 31, 186, 1910.

the first two observations of this series (Fig. 2) the wire was subjected for an instant to a current corresponding to an average field of 50 gausses. The difference in the two plotted points is but a fraction of the experimental error. Neither this test nor any of the other results up to this time gave any suggestion of the effects Walker reports.

TABLE I.

Data for Series 19, Internal Heating.

Length of wire	57.6 cm.
Diameter of wire	.82 mm.
Unvarying load	2109 g.
Added load	2252 g.
Total load per sq. mm.	8.2 kg.

Obs. No.	Time.	Temp.	Stretch.	Current.	No. of Obs.	Young's Modulus $\times 10^{-11}$ Dynes per Cm.^{2}
1	9:30 A.M.	22° C.	.1250 mm.	0.0 amp.	12	19.3
2	10:00	24	.1250	0.0	10	19.3
3	10:20	142	.1280	5.7	10	18.9
4	10:55	263	.1325	7.4	10	18.2
5	11:35	398	.1425	8.5	11	16.9
6	11:50	466	.1650	9.0	5	14.6
7	12:50 P.M.	416	.1445	8.5	10	16.7
8	1:20	340	.1350	7.9	12	17.8
9	2:00	282	.1340	7.4	11	18.0
10	2:45	224	.1325	6.8	11	18.2
11	3:30	168	.1305	6.0	10	18.5
12	4:00	86	.1265	4.0	10	19.1
13	5:00	26	.1240	0.0	11	19.4
14	5:25	77	.1265	3.8	10	19.1
15	5:50	144	.1270	5.6	11	19.0
16	6:50	188	.1305	6.4	10	18.5
17	7:30	230	.1305	7.0	10	18.5
18	7:55	284	.1325	7.6	11	18.2
19	8:20	384	.1360	8.2	11	17.7
20	8:45	408	.1430	8.5	14	16.8
21	9:05	434	.1560	8.7	10	16.0
22	9:30	346	.1370	8.0	11	17.6
23	9:55	244	.1325	7.0	11	18.2
24	10:30	128	.1280	5.0	12	18.8
25	11:00	28	.1240	0.0	10	19.4

It seemed desirable however to employ as large currents as possible in an attempt to bring out the effect. Accordingly the cover of the box enclosing the wire was removed giving the air free access. Series 21, Fig. 3, is the result, the maximum current being 9 amperes, corresponding to a current density of 17 amperes per square millimeter and an average field of 29 gausses. For purposes of comparison series 22 was taken with external heating, the slight tendency of the readings to fall lower (less than .001 mm. difference in the actual measurements) being probably due entirely to the experimental errors caused by the fact that the main part of the apparatus was much hotter in the latter case. No indication of the effects reported by Walker is to be found.

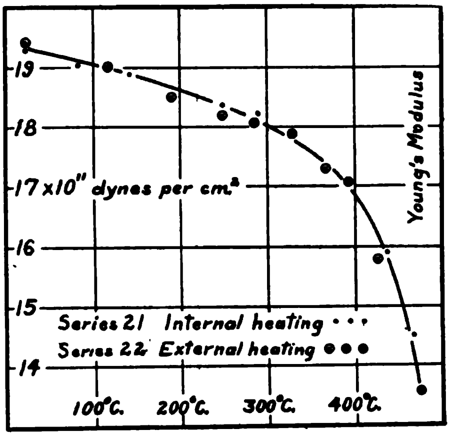

Fig. 3.

Results with internal heating, using the largest possible currents, compared with those with external heating.

Comparison with the Results of Others.

The earlier work[1] upon the effect of an electric current upon Young's modulus is of very questionable value. Reference will be made only to the more recent work of Walker and Miss Noyes. Miss Noyes[2] found no effect peculiar to current in the case of piano wire but her work was not of sufficient accuracy to have revealed even a relatively large difference. Walker,[3] on the other hand, taking measurements with what appears to be a considerably greater accuracy found striking differences of large magnitude. There are several points concerning even his most recent work that make one seriously question whether the results which he secured are attributable to the causes to which they are assigned. A lengthy discussion of Walker's work is out of place at this time but two or three differences in our results may be of interest.

Walker worked over a temperature range of 20° C. to 125° C., finding in the case of iron wire a maximum value of the modulus at about 50° C.,

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[1] Wertheim, Ann. de Chim. et de Phys., *12*, 610, 1844. Edlund, Annal d. Phys., *129*, 15, 1866; *131*, 337, 1867. Streintz, Annal d. Phys., *150*, 368, 1873. Mebius, Oefvers. af k. Vet.-Akad. Forhandl., 681, 1887; Beibl., *12*, 678, 1888.

[2] Phys. Rev., O. S., Vol. 2, 279, 1895; Vol. 3, 433, 1896.

[3] Proc. Roy. Soc. Edin., Vol. 27, 343, 1907; Vol. 28, 652, 1907; Vol. 31, 186, 1910.

the value at 125° C. being about the same as at 20° C. Employing different loads he finds that the maximum is less with the heavier loads amounting to 11.9 per cent. for 18.3 kg. per sq. mm. and only 1.4 per cent. for 32.9 kg. per sq. mm. With steel wire Walker obtains similar results except that at higher temperatures the modulus is a little less than at room temperature and the magnitude of the change in the modulus is smaller. With a load of 23.3 kg. per sq. mm. the maximum value occurs at about 60° C. and is 1.9 per cent. greater than the value at 15° C. For 42.4 kg. per sq. mm. the maximum is at about 35° C. and amounts to 0.3 per cent. The load which I have employed is only 8.2 kg. per sq. mm. It would seem as if some trace of Walker's maximum ought to have appeared, but in my results there has been no indication of any such effect.

Walker[1] also studied the effect of variation of load while keeping the current constant at several different values. For some reason the results are now interpreted in terms of field intensity produced in the wire although formerly the effect of the current was regarded as one of temperature. The fields employed varied from 0.7 to 31.9 gausses for iron and from 0.65 to 33.7 gausses for steel. The loads were 14.6 to 36.5 kg. per sq. mm. and 16.9 to 46.7 kg. per sq. mm. respectively. In each case maximum values of the modulus appeared with intermediate values of both load and field. In the case of iron the maximum variation in the modulus for a given field was 11 per cent., the field being 9.1 gausses and the load 18.3 kg. per sq. mm. The maximum variation for steel was 2.4 per cent. and occurred with a field of 17.4 gausses and a load of 29.7 kg. per sq. mm. As these effects were interpreted as results of magnetic field intensity it is worthy of remark that exactly the same sort of variations were found with the non-magnetic metals copper and platinum.

In my own work the average field intensity is 3.25 times the current in amperes. It varied therefore from 0 to 29 gausses and since the external heating was sometimes used in conjunction it was not always the same for the same temperature. In no instance have I been able to detect any effect peculiar to the current or its accompanying magnetic field and any variation in the modulus amounting to more than one per cent. would have been observed.

Concerning the effect of magnetization upon Young's modulus a great deal of work has been carried on. The more important results have been those of Honda and Terada,[2] Honda, Shimizu, and Kusakabe,[3] Rensing,[4]

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[1] Proc. Roy. Soc. Edin., Vol. 31, 186, 1910.

[2] Phil. Mag., Vol. 13, 36, 1907.

[3] Phil. Mag., Vol. 4, 459, 1902.

[4] Annal. d. Phys., *14*, 363, 1904.

Stevens and Dorsey,[1] Stevens,[2] Brackett[3] and Bock.[4] An effect has been observed but in every case it was small, amounting to less than one half per cent. As far as these results, which are for longitudinal and not circular magnetization, and my own can be compared with those of Walker there is flat contradiction. In the near future I hope to have more data as a basis for comparison. The differences may of course be due entirely to an inherent difference in the samples of wire.

The results of the earlier investigations of the temperature coefficient of Young's modulus of iron and steel wires were over rather limited temperature ranges and were subject to considerable error. Wertheim[5] found for iron a maximum in the neighborhood of 100° C. followed by a rapid decrease up to 200° C. A similar maximum appeared in English steel but not in cast steel. Kupfer[6] employing a method of bending rods found for several metals including iron and steel a decrease of elasticity with increase of temperature. More recently Gray, Blyth, and Dunlop[7] have worked with mild steel and Shakespeare[8] with a "silver" steel wire at room temperature and at or about 100° C. and found a decrease in the modulus per 100° C. of 2.47 and 3.8 per cent. respectively [1.5]. For iron wire the coefficients are 1.6 and 1.8 per cent. respectively while Katzenelsohn[9] reports 2.33 per cent. The bracketed figures here and following are results taken from my own work for corresponding temperatures. The work of Miss Noyes[10] was not sufficiently accurate to have detected other than a linear relation had it existed. She finds for four samples of piano wire with moduli of about 20.3 an average decrease of the modulus of 4.6 per cent. per 100° C.

On the other hand Pisati[11] finds for both iron and steel a decrease of the modulus at an increasing rate for a temperature range extending to 300° C. His value of the modulus for steel is 18.47. Heating from 25° C. to 300° C. produces a decrease of 6.3 per cent. [19.3, 6.7]. For iron the modulus was 21.43, the decrease, 12 per cent. Walker[12] found the modulus of a piece of soft iron wire to be 18.22 at 17.5° C. With ordinary heating up to 129° C. there was a uniform decrease amounting to 3.6 per cent. The

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[1] Phys. Rev., O. S., Vol. 9, 116, 1900.

[2] Phys. Rev., O. S., Vol. 11, 95, 1900.

[3] Phys. Rev., O. S., Vol. 5, 257, 1897.

[4] Annal. d. Phys., *54*, 442, 1895.

[5] Ann. de chim. et de Phys., *12*, 385, 1844; *15*, 114, 1845.

[6] History of Elasticity, Todhunter and Pearson, Vol. II, p. 519.

[7] Proc. Roy. Soc., Vol. 67, 180, 1900.

[8] Phil. Mag., Vol. 47, 539, 1899.

[9] Diss. Berlin, 1887.

[10] *Loc. cit.*

[11] Nuovo Cimento, *4*, 152, 1878.

[12] Proc. Roy. Soc. Edin., Vol. 28, 652, 1907.

modulus of a steel wire was 21.6 at 15° C. It showed a decrease of 2.5 per cent. at 129° C. [19.3, 2.1].

The results of Pisati,[1] Gray, Blyth, and Dunlop,[2] Kohlrausch and Loomis,[3] and Slotte[4] upon the torsion modulus of iron and steel are of interest showing as they do a decrease of the modulus with increase of temperature, the decrease in nearly every case becoming more rapid at the higher temperatures.

DISCUSSION OF ERRORS.

At the lower temperatures the most important source of error is the measurement of the modulus. For temperatures below 350° C. the influence of the temperature upon the modulus is so small that errors in temperature are negligible in comparison. Above 350° C. the temperature effect becomes greater and greater and the errors in the temperature are the more important.

Even with the measurement of the stretch made with micrometer slides accurate to 0.001 mm. it is impossible to be certain of the value of the modulus from any single determination below 350° C. to a greater accuracy than one per cent. In some cases the results vary as much as two per cent. At 350° C. a change in the temperature of 20° C. would be necessary to produce a change of one per cent. in the modulus. At this temperature the measurement of the average temperature is accurate to about 10° C. which is entirely sufficient for the purposes of this investigation.

Above 350° C. the error in the modulus becomes greater amounting to three or four per cent. at 475° C. Over this range the rate of change of the modulus with temperature is so rapid that the errors in the modulus are now negligible in comparison with the temperature error which is perhaps as great as 20° C. at 475° C.

The errors in the modulus are errors of observation and in the plotting of the curves tend to cancel each other. The change of length can be observed to an accuracy corresponding to a temperature difference of one eighth of a degree. The temperature error is therefore due entirely to the difficulty of determining the relation between change of length and temperature, on account of uncertainty as to whether the thermo-couples give the true temperature of the wire. It is probable that this error is not more than 5° C. at 150° C., 10° C. at 350° C., and 20° C. at 475° C. and I am of the opinion that it is considerably less. If we were to con-

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[1] *Loc. cit.*

[2] *Loc. cit.*

[3] Annal. d. Phys., *141*, 481, 1871.

[4] Acta. Soc. Scien. Fennicae, *35*, 1908.

sider the curves as moved, first, with a motion up and down a distance corresponding to one per cent. of the modulus and, second, with a motion to the right and left corresponding to twenty degrees variation in temperature, the true position of the curve would fall well within the area covered.

As explained in a previous section of this paper there is a variation of temperature along the wire amounting to 40° C. at 350° C. Consequently at any given average temperature the value of the modulus is the average of the moduli of elements of length some of which are at temperatures lower and some at temperatures higher than the average. In the case of current heating the variation along the wire is less but a variation in the cross section is introduced. It is assumed that the change of length averages the variation in temperature of the different cylindrical layers as well as the variation along the length. It should be noted that the value of the modulus is a similar average of the moduli of the different layers as well as the different elements of length. Except for the fact that sudden changes in the modulus, or in the slope of the curve, peculiar to some definite temperature would be concealed by this averaging these factors are negligible in comparison with the errors already discussed.

Attention has been called to the effect of magnetization on the modulus and mention is now made of magnetostriction,[1] the cooling of the wire on application of the weight,[2] and the apparent increase in length of the wire accompanying the straightening of the catenary only to call attention to the extreme smallness of these effects and the fact that they may be entirely neglected in this investigation.

SUMMARY.

The results of the tests that have been made upon this sample of mild steel wire may be summarized as follows:

1. The sample showed very erratic changes in elasticity when first heated.

2. By continued heating and stretching it was brought to a cyclic condition, or steady elastic state, in which Young's modulus becomes a function of temperature. This was secured first for a temperature range of 20° C. to 300° C., and later for a range extending to 475° C.

3. Continued heating and stretching gradually increased the modulus, the effect being probably caused largely by the stretching.

4. Except for the small gradual increase above mentioned, the modulus

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[1] Honda and Terada, *loc. cit.* Honda, Shimizu, and Kusakabe, *loc. cit.* Dorsey, Phys. Rev., O. S., Vol. 30, 698, 1910. Brackett, Phys. Rev., O. S., Vol. 5, 257, 1897. Rhoads, Phil. Mag., Vol. 2, 463, 1901, and others.

[2] Joule, Proc. Roy. Soc., Vol. 8, 355, 1857; Phil. Trans., Vol. 149, 91, 1859; Scientific Papers, Vol. I, pp. 405, 413.

of the wire was independent of history, the thermal route by which any temperature was reached having no apparent influence upon the value of the modulus.

5. Heating by an electric current has no effect other than that caused by the accompanying temperature. This is in direct contradiction to the work of Walker. The very small changes in the modulus caused by magnetization reported by other investigators would not have been detected by this apparatus.

6. The Young's modulus of the wire decreased with increase of temperature at an increasing rate. The modulus decreased slowly and almost uniformly up to a temperature of about 300° C. Then the rate of decrease became more and more rapid, the plotted curve becoming very steep at 475° C. The following table is compiled from the various results.

TABLE II.

Change of Young's Modulus of a Mild Steel Wire with Increase of Temperature.

Temperature.	Modulus $\times 10^{-11}$ Dynes per Cm.^{2}	$\frac{dE}{dT} \times 10^{-11}$	Total Decrease, Per Cent. of E at 20° C.	Temperature.	Modulus $\times 10^{-11}$ Dynes per Cm.^{2}	$\frac{dE}{dT} \times 10^{-11}$	Total Decrease, Per Cent. of E at 20° C.
20° C.	19.3	.0035	0.0	300° C.	18.0	.0074	6.7
50	19.2	.0036	0.5	350	17.5	.0106	9.3
100	19.0	.0038	1.5	400	16.8	.0205	11.9
150	18.8	.0041	2.6	425	16.1	.0310	16.5
200	18.6	.0047	3.6	450	15.1	.0470	21.7
250	18.3	.0058	5.2	475	13.8	.0860	28.5

7. The values of the modulus are accurate to one per cent. for temperatures between 20° C. and 350° C. At 475° C. the error may amount to three or four per cent. Below 350° C. the temperature error is negligible in comparison to the error in the modulus. At 350° C. it may amount to 10° C. At higher temperatures the error is greater and of more importance on account of the more rapid decrease of the modulus. At 475° C. it is possible that the error may be as much as 20° C.

8. The above results while applying to but one sample of wire, when considered in the light of other investigations, appear to be characteristic and I should expect to find very similar effects with other samples of iron and steel.

In conclusion I wish to acknowledge indebtedness to the staff of the physical laboratory of the State University of Iowa for their interest in the work and especially to Professor G. W. Stewart for suggesting the problem.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
JULY, 1914.

THERMAL ELECTROMOTIVE FORCES OF IRON OXIDE AND COPPER OXIDE.

By S. Leroy Brown and L. O. Shuddemagen.

THIS work suggested itself when it was noticed that a considerable electromotive force is generated when a cold wire is brought in contact with a similar or dissimilar hot wire. If two iron wires are fastened to the terminals of a galvanometer, one wire heated in a flame and the heated portion is touched with the cool wire, the electromotive force generated is many times sufficient to throw the galvanometer deflection off the scale. If two similar wires are brought together as described above and left in the flame, the electromotive force will reduce to zero or nearly zero; and, if two dissimilar wires are brought in contact and left in the flame, the thermal electromotive force will reduce to the value that is characteristic of the two metals with the hot junction at the temperature of the flame.

These large electromotive forces which are generated when one hot and one cold metal are brought in contact were found to be due to the oxides which formed on the heated metal, and experiments were planned to investigate the thermal electromotive forces at the junctions of oxide and metals. A preliminary report of this work and some values for the thermal electromotive forces of a copper-copper oxide couple were given at the Atlanta meeting of the Physical Society.[1]

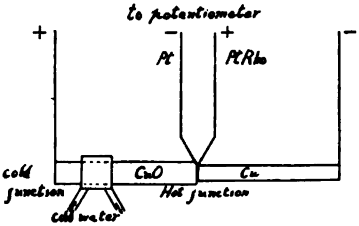

Fig. 1.

The oxides used in these experiments were of solid form and were prepared either by complete oxidation of metallic wires or by melting the oxide and molding into a solid rod. Solid rods of large cross-section were obtained by melting the powdered or finely divided oxides in porcelain tubes which were placed in a tubular electric furnace. In this manner, solid rods of magnetite (Fe_3O_4) and cuprous oxide (Cu_2O), which were from 5 to 15 centimeters long and nearly a centimeter in diameter, were prepared from the molten oxides. The resistances of

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[1] Abstract, Phys. Rev., p. 239, March, 1914.

the oxides are enormous at lower temperatures, and therefore the large rods made possible more accurate measurements of the thermal electromotive forces in the case when an oxide formed one junction of a couple, since the large cross-section diminished the resistance.

The three oxides which were used as thermocouple elements were cupric oxide (CuO), cuprous oxide (Cu_2O), and magnetite (Fe_3O_4). The cupric oxide elements were made from completely oxidized no. 12 copper wires. The cuprous oxide elements were made by melting cupric oxide and quickly cooling from the molten state to a solid as it is molded in a porcelain tube. The high temperature required to melt cupric oxide (CuO) reduces it to cuprous oxide (Cu_2O) and, if quickly cooled to a temperature below 800° C., solid cuprous oxide is obtained. If this solid is heated to about 800° C. it will decompose into free copper and cupric oxide. The magnetite elements were obtained by melting iron oxide and molding in porcelain tubes. The temperature to melt the iron oxide (Fe_2O_3) reduces it to magnetite (Fe_3O_4) and the solid formed from the molten state is solid magnetite.[1]

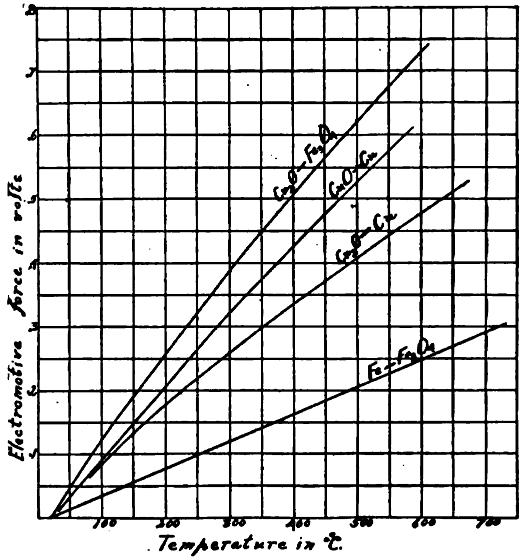

Fig. 2.

Thermal Electromotive Force Curves.

The thermal electromotive forces of the oxides were measured with a

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[1] The authors are indebted to Mr. D. J. Brown, of the School of Chemistry, University of Texas, for analyses of these oxide elements which were found to be of the chemical composition as indicated in this paper except that the cuprous oxide element contained a small per cent. (1.5) of cupric oxide.

potentiometer, and the temperatures of the hot junction were measured with a standardized platinum-platinum rhodium thermocouple while the cold junction was maintained at room temperature. The junction of a metal and an oxide or of two oxides was made as shown in Fig. 1, the junction of the standard thermocouple being at the junction of the couple which was being investigated. A cooler through which water circulated maintained the cooler end of the oxide element at room temperature, while the hot junction was heated by means of a flame or an electric heating coil. The electromotive forces of the junction which was being examined were recorded only when the standard thermocouple indicated that the temperature of the junction was remaining approximately constant.

The following data and curves show the thermal electromotive forces

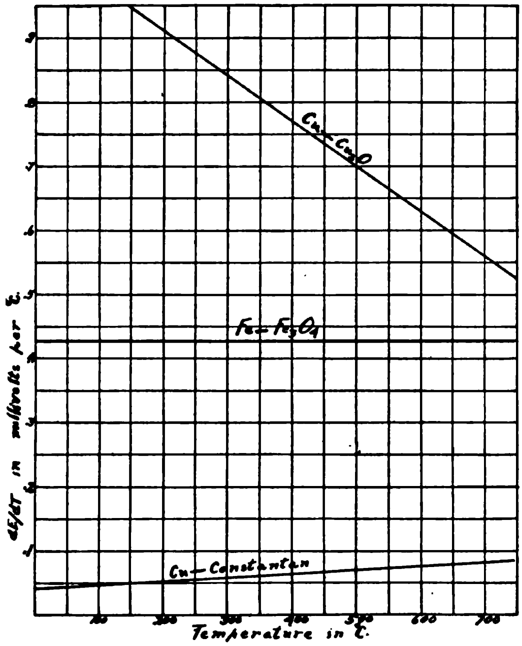

Fig. 3.

Thermo Electric Power Diagrams.

for copper-cupric oxide, copper-cuprous oxide, iron-magnetite, iron-cuprous oxide, copper-magnetite and cuprous oxide-magnetite thermocouples with temperatures of the hot junction ranging as high as 750° C. The data shows no appreciable difference, between the copper-cuprous oxide and iron-cuprous oxide couples, or between iron-magnetite and copper-magnetite couples. The electromotives forces as determined for the cuprous oxide-magnetite couple could not be accurately measured on account of the extremely high resistance of a junction of two oxides but the data obtained gives points which lie near the curve which is obtained by an addition of the two metal oxide curves.

The electromotive force variation with temperature of a copper-cuprous oxide couple can be approximately expressed by the parabolic relation,

$$e = 1.0375(t - 20) - .000375(t - 20)^2 \text{ millivolts}$$

when the cold junction is at 20° C., or the thermo-electric power of this couple is

$$de/dt = 1.0375 - .00075(t - 20) \text{ millivolts per degree C.}$$

The electromotive force curve for the iron-magnetite couple is very accurately represented by the linear relation,

$$e = .427(t - 20) \text{ millivolts,}$$

or its thermo-electric power is

$$de/dt = .427 \text{ millivolts per degree C.}$$

The thermo-electric power lines for these two couples and a copper-constantan couple (for comparison) are shown in Fig. 3.

After several reheatings of a junction which has a cupric oxide element, its electromotive force will diminish and its electromotive force curve will approach the curve that is obtained when the cupric oxide element is replaced by cuprous oxide. That is, the higher temperature partially reduces the cupric oxide to cuprous oxide. When cuprous oxide is one of the elements of a couple, the junction cannot be subjected to temperatures higher than about 800° C. without decomposition, and this decomposition is accompanied by a decided decrease of thermal electromotive force.

The thermal electromotive forces developed by the above described couples are to the authors' knowledge very much larger than have been noted by previous experimenters. Weiss and Koenigsberger[1] noted a large thermal electromotive force for a junction of a metal and magnetite ore but their experiment was not carried to temperatures higher than 100° C. Bäedeker[2] measured the thermal electromotives forces for several metallic sulphides and oxides but only through a very small temperature range. Since the data in this paper were taken, an article has been published by C. C. Bidwell[3] which describes a very extensive research on thermal electromotive forces of oxides and which includes cupric oxide

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[1] Phys. Zeitschr., *10*, p. 956.

[2] Ann. der Phys., *22*, 4, p. 749.

[3] PHYS. REV., March, 1914.

and magnetite. The values found by the authors for these two oxides are very much larger than the values found by Bidwell. This may possibly be accounted for by a difference in the preparation of the elements and hence different physical states. As stated before, the authors resorted to chemical analyses to make sure of the chemical compositions of the molten products which were used as thermocouple elements.

The cold junction was maintained at room temperature or approximately 20° C. for all the following data.

$(\mathrm{Cu})_{-} - (\mathrm{Cu\,O})_{+}$[1]		$(\mathrm{Cu})_{-} - (\mathrm{Cu_2\,O})_{+}$		$(\mathrm{Fe})_{-} - (\mathrm{Cu_2\,O})_{+}$	
Hot Jc., °C.	**E.M.F., Volts.**	**Hot Jc., °C.**	**E.M.F., Volts.**	**Hot Jc., °C.**	**E.M.F., Volts.**
95	.090	95	.078	100	.085
132	.135	152	.130	322	.280
187	.192	168	.148	497	.410
217	.226	177	.158	538	.434
252	.267	192	.168	642	.503
305	.330	236	.209		
325	.345	297	.261		
351	.375	305	.265		
375	.398	348	.296		
395	.422	407	.345		
445	.473	466	.388		
503	.524	527	.427		
525	.552	595	.474		
548	.573	665	.518		
570	.591	710	.542		

$(\mathrm{Fe})_{+} - (\mathrm{Fe_3\,O_4})_{-}$		$(\mathrm{Cu})_{+} - (\mathrm{Fe_3\,O_4})_{-}$		$(\mathrm{Cu_2\,O})_{+} - (\mathrm{Fe_3\,O_4})_{-}$	
90	.030	102	.035	92	.112
175	.067	113	.041	155	.200
265	.104	240	.097	210	.276
300	.120	315	.125	280	.345
362	.144	357	.145	312	.405
404	.163	423	.175	405	.515
468	.190	550	.225	492	.602
517	.211			613	.745
565	.231			651	.770
588	.240				
602	.246				
640	.278				
670	.288				
693	.300				
725					

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[1] Each parenthesis represents an element of the couple and the positive or negative subscripts represent the polarity.

THE TOTAL LUMINOUS EFFICIENCIES OF PRESENT-DAY ILLUMINANTS.

BY HERBERT E. IVES.

LIGHTING science has lagged behind other branches of engineering in the definiteness of its quantitative aspects and in exactness of terminology largely through the chaotic condition of the question of luminous efficiency.

While the efficiency of a motor or a transformer may be derived in the form of a definite fraction or percentage from the direct comparison of output to input, both measured in the same units, the efficiency of an illuminant has not been so expressible. The engineer, who measures input in watts, and luminous output in lumens, expresses efficiency in lumens per watt, a ratio of value in comparing one illuminant with another, but one whose unit is very far from being the ideal efficiency which is understood by 100 per cent. efficiency in any other connection. The so-called "luminous efficiencies" to be found in physical literature might with greater propriety be called the "visible fractions" of the radiated power. They are expressed in percentage values, but the unit is not the most efficient illuminant—it is the most efficient illuminant possessing the same visible spectrum as the one measured. It affords no exact measure of comparison of one illuminant against another.

The unravelling of this tangle is attained by so defining luminous flux that its dimensions are the same as power, and by determining the constant of proportionality between the present arbitrary luminous flux unit and the power unit. These two steps have been taken in the definition of luminous flux as "radiant power evaluated according to its capacity to produce the sensation of light," and in the determination of the ratio of the lumen to the watt, recently published in this journal.[1] With these steps taken it is a simple matter to arrive at the luminous efficiency of any illuminant, given its power input, its power output, and its luminous output. It is only necessary to transform the last quantity from lumens to the equivalent watts, to have all the quantities in the same units. Then we have,

$$\frac{\text{Luminous output}}{\text{power input}} = \text{total luminous efficiency;}$$

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[1] PHYS. REV., The Mechanical Equivalent of Light.

$$\frac{\text{Luminous output}}{\text{radiant power output}} = \text{radiant luminous efficiency.}$$

Radiant luminous efficiency may be determined, as indicated, by knowledge of the radiated power and the watt value of the lumen. It can however be found much more simply by the measurement of the ratio of light-evaluated to unevaluated power. Measurements of this quantity have been made in this way by Karrer and reported in this journal.[1]

For the determination of total efficiency, on the other hand, it is necessary to measure each quantity in question, since different instruments and methods are required for each. It is here that the recently determined value of the lumen in terms of the watt is indispensable, and it is with this quantity alone that the present paper deals.

The lumen has been found to be .00162 watt. The "efficiency" of any illuminant in lumens per watt can, by the use of this constant, be translated into *watts of luminous flux per watt of power input.*

This is a simple fraction, on a scale of efficiency in which the value of the most efficient possible light source is unity.

An illustration will make clear the derivation of the values for total luminous efficiency given in the table. The standard carbon incandescent lamp has an efficiency in the present practical units of 2.59 lumens per watt. Now $2.59 \times .00162 = .0042$, the ratio of luminous output to power input expressed in the same units, or the total luminous efficiency. The construction of a table of total luminous efficiencies thus involves no more arduous labor than the multiplication of the lumens per watt of the illuminants of interest by a constant, that constant being the watt value of the lumen. If the watt is adopted as the unit of luminous flux, as the writer has suggested, the ratio of output to input as measured is at once the efficiency. The superiority of the watt over a unit based merely on a certain combination of wick and wax should not require much discussion.

In the case where the power consumption is expressed in a unit other than the watt, a prelimination transformation to watts should be made, or the corresponding constant may be worked out. Thus gas illuminant efficiencies are commonly expressed in "lumens per British thermal unit per hour." This may be reduced to lumens per watt by dividing by .293, or it may be reduced at once to total efficiency by multiplication by .00162/.293 or .00553.

The appended table of total luminous efficiencies has been prepared from data collected from a number of sources. A few figures are calculated from the very full table in Liebenthal's Praktische Photometrie where

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[1] Phys. Rev., March 1915, p. 189.

Illuminant, Commercial Description.	Commercial Rating.	Efficiency in Present Units (Lumens per Watt).	Ratio $\frac{\text{Watts of Luminous Flux}}{\text{Watts Input}}$ or Total Efficiency on Correct Scale.
Carbon incandescent lamp Oval anchored (treated) filament.	4-watts per mean hor. C.P.	2.6	.0042
Tungsten incandescent lamp Vacuum type.	1.25 watts per hor. C.P.	8	.013
Mazda, Type C	600 C.P.-20 amp. .5 w.p.c. Series type C.	19.6	.032
	500 watt, multiple, .7 w.p.c. Type C.	15	.024
Carbon Arc Open arc.	9.6 ampere; clear globe	11.8	.019
Enclosed arc Light opal inner; clear outer and street reflector.	6.6 ampere, D.C.	5.9	.0096
Series enclosed carbon arc; light opal inner; clear outer; street reflector	7.5 ampere, A.C.	5.6	.0091
Magnetite arc Series luminous arc lamp; ornamental type; clear globe; standard electrodes.	6.6 ampere, D.C.	21.6	.035
Enclosed white flame carbon arc	10 ampere, A.C.	26.7	.043
	6.5 ampere, D.C.	35.5	.058
Enclosed yellow flame carbon arc	10 ampere, A.C.	31.4	.051
	6.5 ampere, D.C.	34.2	.055
Open arc, white flame, inclined trim	10 ampere, A.C.	29	.047
	10 ampere, D.C.	27.7	.045
Open arc, yellow flame, inclined trim	10 ampere, A.C.	41.5	.067
	10 ampere, D.C.	44.7	.072
Moore Nitrogen Vacuum Tube	220-volt, 60-cycle, tube length 113.17 feet	5.21	.0085

Illuminant, Commercial Description.	Commercial Rating.	Efficiency in Present Units (Lumens per Watt).	Ratio Watts of Luminous Flux / Watts Input or Total Efficiency on Correct Scale.
Quartz Mercury arc[1]	174–197 volt; 4.2 ampere	42	.068
Glass Mercury arc[1]	40–70 volt; 3.5 ampere	23	.037
Nernst lamp[1]		4.8	.0077
Acetylene[1]	1.0 liters per hour consumption	.67	.0011
Petroleum lamp.[1]		.26	.0004
Incandescent gas lamp (low pressure)	.350 lumens per B.t.u. per hr.	1.2	.0019
Incandescent gas lamp (high pressure)	.578 lumens per B.t.u. per hr.	2.0	.0032
Open flame gas burner	Bray 6' high pressure	.22	.00036

[1] = figures from Liebenthal's Praktische Photometrie.

they are given in Hefner lumens per watt. The figures for the more recent illuminants have been collected from authoritative sources to whom acknowledgment is made below.

A difficulty in the collection of such data lies in the common practice of publishing efficiencies in terms of horizontal or hemispherical watts per candle, instead of mean spherical. The latter is of course the only value of use in calculating total efficiencies.

It is at once obvious from these figures that light is at present only a by-product. The highest efficiencies tabulated are those of the mercury arc in quartz and the yellow flame arcs. In both cases, however, the figures are misleading, because the overall efficiency is much reduced by the steadying resistances which are indispensable for the practical operation of these light sources.

The highest present efficiencies of light production do not exceed probably 5 per cent. of what should be possible.

Perfect efficiency on this scale of course means monochromatic green light. But even if the most efficient continuous spectrum *white light* is taken as the goal, this present 5 per cent. is increased only to 5/.40 or 12.5 per cent., the most efficient white light being about 40 per cent. efficient.[1]

It is of interest to compare these total efficiencies with the corresponding radiant efficiencies as determined by Karrer. The ratio:

$$\frac{\text{total efficiency}}{\text{radiant efficiency}} = \frac{L/P}{L/R} = \frac{R}{P}$$

(L = luminous flux, P = power input, R = radiant power) gives the *radiation efficiency* or fraction of the applied power which is transformed into radiation.

Now in the case of the carbon vacuum incandescent lamp the radiation efficiency = .0042/.0045 or over 90 per cent., while in the case of the incandescent gas burner this ratio is .0019/.012 = .16; in other words five-sixths of the applied power is lost as convection and conduction.

The writer takes pleasure in acknowledging his indebtedness to Mr. S. L. E. Rose, Mr. T. H. Amrine and Mr. R. B. Chillas for data on the electric illuminants.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.

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[1] Ives, Electrical World, June 15, 1911.

THE NATURE OF ELECTRIC CONDUCTION AS REQUIRED TO EXPLAIN THE RECOVERY OF RESISTANCE OF METALLIC SELENIUM FOLLOWING ILLUMINATION.

By F. C. Brown.

DIFFERENT theories have been proposed to explain the transportation of electricity in solids, but metallic conductors generally have not offered satisfactory evidence for a final decision between the theories. The illuminating experiments on thermionics by Richardson and his students and also the consistent agreement of theory and experiment involving the ratio of the electrical to the thermal conductivity of metals have made various modifications of the dynamical equilibrium theory very popular. The seemingly most contradictory evidence to this theory is the low value of the specific heat for all the metals. However, Sir J. J. Thomson[1] has shown that the calculated and experimental ratios of the electrical to the thermal conductivity may agree equally well by a theory that presumes the electrons to be tied up with the atom in the form of a doublet. In this case electric conduction would be merely the transportation of electron from doublet to doublet much in the same way as the Grotthus chains in the old theory of electrolysis.

I shall in this paper present information which leads away from the first mentioned view above and which forms the basis for a theory bearing more or less resemblance to the above mentioned second theory of Thomson. For the reason that the conducting power of metallic selenium crystals may be varied by so many physical conditions, we have the obvious opportunity of making very definite choice as to what form of the electron theory is satisfactory. Having obtained a consistent theory for selenium, we can then decide if reasonable modifications of the theory will explain conduction in the other elements, where there are less favorable means of attack.

The investigations described in this and succeeding papers will be somewhat along the line of attack made by J. W. Nicholson.[2] An effort will be made to choose experiments that enable decision to be made with

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[1] Book on the Corpuscular Theory of Matter, 1907.

[2] Phys. Rev., N. S., Vol. 3, p. 1, 1914. See also article by Merritt, Phys. Rev., 25, p. 505, 1907, which involves some of the elements of the ideas in this paper.

a minimum number of assumptions. The author is not aware of any direct or indirect measurements having been made which consider any particular value for the rate of recombination of electrons with their positive residues, except in the conduction of electricity through a gas under the influence of an ionizing agent. The subject will be opened by a consideration of the rate of recombination of the electrons and some of the conditions that influence this rate.

THEORETICAL CONSIDERATIONS.

It will be assumed that the specific conductivity varies as the number of electrons taking part in the conduction at any instant. The electrons do not exist free in the sense of the kinetic theory of gases. Under illumination they are rendered unstable or free but on the average they recombine with the atomic structures very rapidly. Experiment shows that following intense illumination thirty per cent. of the extra electrons return to their fixed positions in .02 second. A second assumption that will be made is that the recombination of the freed electrons will take place according to the same law governing the recombination of ions in gases. Then the rate of recombination of electrons will be expressed as,

$$\frac{dN}{dt} = -\alpha N^2, \tag{1}$$

where N is the average number of electrons in the free state at any instant and α is the coefficient of recombination. However, this equation holds only for a uniform distribution of the electrons. Such a distribution would exist when the selenium reaches the equilibrium condition in the light, or for the first small interval of time, Δt, after the illumination is shut off. The theory will presuppose that the coefficient of recombination is not altered by the condition of light or dark, and the experiments will verify this presumption.

Since the conductivity is proportional to the number of free electrons, we may write,

$$i = k_1 \cdot N \tag{2}$$

from which it follows that

$$\frac{di}{dt} = -\frac{\alpha i^2}{k_1}, \tag{3}$$

or

$$\frac{di}{dt} = -\alpha' i^2,$$

where α' is merely a new constant.

When the selenium is in equilibrium in the light the rate of recombination of the electrons is exactly equal to the rate of production of electrons by the light in addition to the natural production in the dark. This may be represented as

$$\frac{dN}{dt} = M + q,$$

or

$$\frac{di}{dt} = k_1(M + q), \tag{4}$$

where M is the former rate and q is the latter or dark rate. Combining equations (3) and (4) we obtain, for the equilibrium value of the current,

$$i_e = k_1\sqrt{\frac{M + q}{\alpha}}. \tag{5}$$

Now we could check the theory by the application of observed data to satisfy equation (5), but the rate of production of electrons by light, M, is dependent upon the light intensity and therefore it will be more convenient to test the adequacy of the equation in the next succeeding paper, together with the law governing the rate of production with varying light intensities. It will be the purpose of this paper to verify the fundamental relation of rate of recombination to the number of free electrons, as expressed in equations (1) and (3). It was found that equation (3) could be verified when expressed in the approximate form

$$\frac{\Delta i}{\Delta t} = - \alpha' i^2, \tag{3}$$

when Δt was kept a very small interval of time and constant. Ordinarilly we should expect to check this equation by the application of its integrated form,

$$\left(\frac{1}{i} - \frac{1}{i_0} = \alpha t\right)$$

to a complete recovery curve extending over a considerable length of time. However, I have found that this can not be carried out satisfactorily because as soon as a large percentage of the electrons have recombined, a non-uniform distribution of the electrons and uncombined atoms exists, such that the coefficient of recombination is diminished. But it is not essential to the argument of this paper to either prove or disprove this statement. A slow diffusion of the electrons, and changing crystalline structure, no doubt are complexities to be taken into account in explaining a complete recovery curve.

That equation (3) is tenable, together with the underlying assumptions mentioned, may be ascertained from some observations taken with masses of crystals some years back. In my paper on the "Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium"[1] on p. 415

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[1] Phys. Rev., Vol. 33, p. 403, 1911.

is just such data as desired. The conducting component, B, has the same significance as i or N in this paper. The recovery during the mean interval of .05 second was measured after the selenium had begun to recover from illumination of varying intensities. The varying intensity produced the varying conductivity noted in the following table.

Conductivity in Dark. i_0	Conductivity in Light. i	Change of Conductivity, Ohms^{-1}. $\Delta i = k \cdot N$	$\frac{\Delta i}{i}$	$\frac{\Delta i}{i^2}$	Coefficient of Recombination. $\alpha' = \frac{\Delta i}{i^2 t}$
1.47×10^{-6}	6.29×10^{-6}	0.016×10^{-5}	2.5×10^{-2}	4.0×10^3	80×10^3
	13.5 × "	0.11 × "	8.2 × "	5.9 × "	118 × "
	60.2 × "	2.79 × "	46.5 × "	7.6 × "	152 × "
	35.4 × "	1.05 × "	29.6 × "	7.9 × "	158 × "
	50.8 × "	2.04 × "	40.2 × "	7.4 × "	159 × "
	16.1 × "	0.18 × "	11.2 × "	6.9 × "	138 × "

It may be observed, where the change of conductivity varies over the extreme range of from .016 to 2.79 (*i. e.*, by a factor of 174) that $\Delta i/i^2$ is approximately a constant. The values of α' as recorded in the last column are slightly in error because no allowance is made for the liberation of electrons taking place in the dark simultaneously with their recombination. If no new postulates are involved this correction should be of magnitude, $(i_0^2 \cdot \alpha' \cdot \Delta t)$, when added to Δi for the calculation of α'. Since this correction involves an error of less than ten per cent. in any value above, we will not complicate the argument of this paper by the application of this correction or considerations of the adequacy of the correction. Since the range of application of the data is so great, we may regard the constancy of the coefficient of recombination as satisfactory evidence that the electrons recombine with the atomic structures in accordance with the conception involved in equation (1), when the conditions are as specified. Since writing this paper I have also verified this fundamental conception by experiments on the recovery of single isolated crystals of selenium. This agreement of behavior of crystals and crystal aggregates is quite consistent with the other unique properties existing in the crystals, such as the likeness of the wave-length,—sensibility curves.[1]

It may be noted that a constant coefficient of recombination involves the idea that the number of electrons freed in dark recombine at a more rapid rate, when the selenium is illuminated or just following illumination. This follows because there are more positive residues and consequently more chances for recombination.

It should also be noted that Plimpton[2] has observed that ions in gases

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[1] PHYS. REV., N. S., Vol. 4, p. 507, 1914; Vol. 5, p. 65, 1915.

[2] Am. Journ. of Sc., Vol. 35, p. 39, 1913.

also recombine according to the same law involved in equation (1), only in case there is a uniform distribution of ions. However, this agreement of the law of recombination of electrons in selenium with the recombination of ions in gases does not further lead us to suspect that the electric current may be transported by the same method in both selenium and in gases. The current in selenium with a given low potential is infinitely larger than any ionization current in gases, except in spark discharge. Further differences and likenesses of the method of transportation of the current will be brought out in later developments of the theory.

The Inadequacy of Ohm's Law.

A fundamental property in metallic selenium exists in the inadequacy of Ohm's Law to explain the variation of the current with the applied voltage. In all cases the current increases more rapidly than the proportional increase of the voltage. It is therefore pertinent to inquire what conditions are responsible for this unique property. According to the theory involved in equation (5) an increased potential can vary the specific conductivity only in two ways, by varying the rate of production of the electrons or by varying the rate of recombination of the electrons.

We will suppose that the increase of current necessary to satisfy Ohm's Law, when the voltage is increased, arises from increased velocity of drift of the electrons, and that the slight excess current arises from additional electrons in the conducting state. This increased number might come either from a magnified rate of production or from a diminished rate of recombination.

The increased rate of production might be expected because of bombardment of semi-fixed electrons by the faster moving ones or the greater electric intensity might be considered as lowering the degree of stability of all the electrons of a certain class in the atomic structure. Consistent with either of these views, it would be reasonable to expect a diminished rate of recombination as the voltage is increased. An increased velocity of drift would lessen somewhat the chance of an atom to capture an electron and also a lower stability of the atom would indicate a smaller attractive force for the electron.

A measurement of the recovery during a short interval following the extinction of the illumination should determine whether the coefficient of recombination varies with the applied potentials in such a manner as to explain the inadequacy of Ohm's Law.

The change of conductivity during short periods of recovery was measured by the Wheatstone's bridge and pendulum method.[1] The light

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[1] Phys. Rev., Vol. 33, p. 54, 1911.

was cut off the selenium at the desired time by an aluminum shutter attached to the timing pendulum. A single lamellar crystal of metallic selenium of the fifth system was used for this investigation. The intensity of illumination from which the crystal recovered was kept constant. Also the pressure on the crystal was fixed at such a value that the resistance was 1,349,000 ohms with 1.45 volts. The change of conductivity was measured for the first 0.05 second interval of recovery, both when 1.45 volts was the difference of potential across the crystal and when there was 20 volts.

The change of conductivity during recovery of 0.05 seconds is shown in the following table. For convenience 0.05 second is here considered as the unit of time.

	With 20 Volts.	With 1.45 Volts.
Resistance in dark	1,192,000	1,349,000
Resistance in unvarying light	356,000	392,000
Conductivity in light	$i = 28.1 \times 10^{-7}$	$i = 25.5 \times 10^{-7}$
Recovery after 0.05 second	$i = 15.65 \times 10^{-7}$	$i = 14.1 \times 10^{-7}$
Change of conductivity	$\Delta i = 12.5 \times 10^{-7}$	11.4×10^{-7}
$\alpha' = \frac{\Delta i}{\Delta t \cdot i^2}$	1.58×10^5	1.75×10^5
$\frac{\alpha'}{i} = \frac{\Delta i}{i} = \frac{\Delta N}{N}$	0.447	0.447

It may be observed that the coefficient of recombination is not constant. In fact a brief consideration of the data reveals that this coefficient varies directly as the specific resistance of the crystal, when the variation of the specific resistance accrues from an altered potential difference between the crystal electrodes. This conclusion is verified by the constant ratio of α'/i, as recorded in the last row above.

If the constant, α', were the sole quantity that changed its value with varying potentials across the crystal, then we might expect in accordance with equation (5) that the equilibrium light sensitiveness of the crystal would vary inversely as the square root of α. However, the data for the same crystal that is given in the following table shows that the equilibrium light sensitiveness is almost proportional to the conductivity in the light. Since (α) varies inversely as the same conductivity in the light, and since the conductivity is influenced only by the square root of the recombination constant, it follows that the light sensitiveness should, according to equation (5), vary directly by some function of $M + q$, and further that this function should have the same value as the function relating (α) to the conductivity. This idea is a little beyond the province of this paper and will need to be verified further.

Potential across the crystal in volts	1.5	6.0	36	60
Conductivity in dark	5.9×10^{-7}	6.0×10^{-7}	6.85×10^{-7}	7.5×10^{-7}
Conductivity in light	20×10^{-7}	20.4×10^{-7}	23.3×10^{-7}	24×10^{-7}
Equilibrium light sensitiveness	14.1×10^{-7}	14.4×10^{-7}	16.5×10^{-7}	$16.5 - 10^{-7}$
$\frac{\text{Light sensitiveness}}{\text{Conductivity in light}}$	.705	.70	.70	.69

The Pressure Effect.

The increase of the specific conductivity of selenium, by pressure, whether in isolated crystals or crystal aggregates is another unique principle that our electron theory should explain.[1] The specific conductivity may vary a hundred fold by increasing the pressure. According to the postulates in the earlier part of the paper, this increase of conductivity must arise either from an increase in the number of electrons capable of taking part in the conduction or in a decrease in the ratio of recombination of the electrons with the positive residues. From a consideration of the increase of the absolute light sensitiveness with increased pressure I have already concluded[2] that it would be unreasonable to expect the light-sensitiveness to increase in proportion to the conductivity in the dark, if the conductivity must vary alone with the number of electrons liberated.

Since there is no reason to expect any large changes of conductivity resulting from variations in the free path of the electron, it seemed very plausible that pressure might alter the rate of recombination of the electrons.

In the experimentation, the selenium crystal was placed between brass electrodes and the variable pressure desired was controlled by a screw adjustment. At each pressure the equilibrium conductivity was measured both with the crystal in the dark and with constant illumination. The recovery was measured during the first mean period of .02 second after the extinction of the illumination as elsewhere described. A constant difference of potential of 13 volts was kept between the crystal electrodes. The equilibrium conductivity in the light was attained in less than a second after illumination.

The following table shows the value of the coefficient of recombination for various pressures on the crystal such that the conductivity varied from 1.79×10^{-7} to 23.8×10^{-7} in the dark.

Since the pressure effect is of such large magnitude as noted, we may conclude (from the constant value of $\alpha' \cdot i$) with some certainty that the

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[1] Brown and Stebbins, Phys. Rev., Vol. 26, p. 273, 1908; Phys. Rev., N. S., Vol. 4, p. 85, 1914.

[2] *Loc. cit.*, article above.

Pressure.	Conductivity		Recovery in .02 Sec. Change of Conductivity. $i = K \cdot N$	$a' = \frac{\Delta i}{i^2 \cdot \Delta t}$	$a' \cdot i$
	in Dark Ohms^{-1}.	in Light Ohms^{-1}.			
P_1	1.79×10^{-7}	5.18×10^{-7}	1.84×10^{-7}	3.5×10^7	17.9
P_2	6.50 × "	15.4 × "	4.12 × "	1.35 × "	17.1
P_3	12.2 × "	30.3 × "	9.02 × "	0.445	14.2
P_4	18.9 × "	43.9 × "	14.36 × "	0.300	15.0
P_5	23.8 × "	55.5 × "	15.5 × "	0.26	14.0

coefficient of recombination varies inversely as the initial conductivity in the light, that results from the pressure.

Now it may be observed in the same table of data that the light sensitiveness at the different pressures is almost proportional to the conductivity in the dark accompanying each pressure. If, in equation (5), the value of q were small compared with M, it would be necessary for M (the rate of production by a fixed illumination) to vary directly with the initial conductivity at any pressure in order that this increase of light sensitiveness might be proportional to the dark conductivity.

We have, therefore, proved that the coefficient of recombination varies inversely as the conductivity ensuing from the pressure, and the evidence just stated inclines very much toward the view that the rate of production by light varies directly as the same conductivity resulting from the pressure effect.

GENERAL CONSIDERATIONS.

The attempt has been made to build up a simple electron theory to correlate the most fundamental photo-electro-mechanical properties in metallic selenium. The experiments have been carefully selected to verify the basic conceptions with a minimum number of postulates, by avoiding all questions of absorption, reflection and time rate of change of conductivity.

The effort has been successful in achieving a simple consistency of results. It was first shown that the electrons do recombine very rapidly with what is supposed to be the atomic structures, and the recombination takes place according to the same law governing the recombination of ions in gases. But we can not conclude from this that the current is transported in the same way in selenium as an ionization current in gases.

The basis of the theory receives further support in that a common explanation accounts both for the variation from Ohm's law and for the large changes of conductivity accompanying pressure changes. In each case the coefficient of recombination of the electrons is found to vary inversely as the variable conductivity imposed by the pressure change or the difference of potential. And likewise, there is common evidence that the rate of production of conducting electrons by a fixed illumination is directly proportional to the variable conductivity imposed by pressure or voltage.

The temporary liberation of electrons by light bears certain resemblance to the original suggestion of Pfund[1] in which he compared light-action in selenium to an internal photo-electrical effect. This idea also is consistent with the experiments of Dr. L. P. Sieg and the author[2] where we have found all isolated crystals of selenium to have a maximum sensibility in the ultra-violet region of the spectrum.

But the experiments indicate a distinctly new idea as involved in a coefficient of recombination of the electrons that varies with the physical conditions surrounding the crystal, and also a varying rate of production of electrons with a fixed light intensity. This varying rate of freeing of electrons is governed by the same law apparently as that governing the variation of the recombination constant, except that the two relations are in inverse direction.

The form of the electron theory as here presented offers a satisfactory explanation of the electro-dynamical, light-electrical and electrical relations recently published.[3] The action due to pressure is not transmitted beyond the region of stress. The pressure merely lowers the stability of the selenium such that a given light intensity may liberate a greater number of electrons where this stress exists and such that the electrons recombine less rapidly in the same region.

Consistent with this interpretation, the light action transmitted to a distance is increased if the pressure is applied to the portion of the crystal where the conduction takes place, but the transmitted effect is not increased by pressure applied only at the place of illumination. The transmitted light action is of the nature of a crystal disturbance, which lowers the stability of the electrons everywhere in the confines of the crystal.

Since the analysis has shown the voltage effect to be identical with the pressure effect so far as the rate of recombination of electrons or their liberation is concerned, it is to be expected that the voltage effect could not be transmitted throughout the crystal in the way that light action is transmitted. This, in fact, is the result found in the previous work.[4]

Naturally the theory suggests many other lines of investigation in order to obtain more detailed information as to the nature of electric conduction in selenium. Since we have already considered such a wide range of experiments and have obtained such satisfactory agreement, the theory is one of unusual promise.

[1] Phys. Rev., Vol. 28, p. 234, 1909.

[2] Phys. Rev., Vol. 4, p. 48, and p. 507, 1914.

[3] Phys. Rev., N. S., 1914.

[4] *Loc. cit.*

SOME EXPERIMENTS ON THE NATURE OF TRANSMITTED LIGHT-ACTION IN CRYSTALS OF METALLIC SELENIUM.

BY F. C. BROWN.

RECENTLY we showed[1] that light falling on one part of a crystal of selenium would produce a change of conductivity throughout the crystal. In the acicular crystals this effect was observed practically undiminished in amount as far as 10 mm. away from the point of illumination. This effect was denoted by the authors as a new property in matter. The work described in this paper consists essentially of two investigations designed to give information concerning the nature of this light-action. The first was an experiment to determine the velocity of transmission of the light effect along the crystal, and the second was a study of certain interrelated phenomena between the pressure effect[2] and the transmitted light action. The one showed the action to be transmitted much too rapidly for a temperature effect. The other definitely proved that the increase of conductivity at a distance could not arise from transmitted free electrons. Incidently, the results call forth a new view as to the nature of electrical conduction as exhibited in crystals of metallic selenium.

THE RATE OF TRANSMISSION OF LIGHT-ACTION ALONG THE CRYSTALS.

To obtain information as to the rate of transmission of this new effect the method used was to determine the resistance after short intervals of time following illumination at a distant point. A lamellar crystal of the fifth system, of size about 4 × .6 × .3 mm., with striations perpendicular to the length of the crystal was mounted with opposite ends between separate sets of electrodes as shown conventionally in Fig. 1. Under crossed nicols the crystal would show parallel extinction. A constant source of illumination was obtained by focussing a Nernst glower on the crystal.

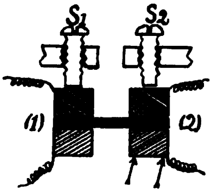

Fig. 1.

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[1] Brown and Sieg, Phil. Mag., Ser. VI., Vol. 28, p. 497, 1914; Brown, PHYS. REV., N. S., Vol. IV., p. 85, 1914.

[2] For a description of this effect see paper by author in PHYS. REV., Ser. 2, Vol. 14, p. 85, 1914.

The procedure was to connect the resistance between electrodes at end (2) in one arm of a Wheatstone's bridge circuit. The resistance of this part of the crystal was measured in the dark and when it was illuminated, and then the same part was measured again when the opposite end (1) was in the dark and then in equilibrium under the same constant illumination as was previously on the conducting end. Next the above procedure was repeated several times, with the modification necessary to measure the change of resistance during the first 0.4 second of illumination. The object was to determine what part of the total change of resistance was transmitted two millimeters along the crystal in this short interval. Of course, even if the light falls directly on the part of the crystal whose resistance change is under determination all the effect does not take place at once.[1] Thus the opposite ends of the crystal were illuminated alternately in order to find the relative lag in the transmitted effect.

The method of measuring the change of resistance in these small intervals was that described by Brown and Clark.[2] A shutter was attached to a ballistic pendulum, which automatically put a galvanometer in circuit for a short interval at any desired time after the shutter moved out of the path of the beam of light directed on the crystal. Thus in Table I. the change of resistance was recorded as divisions throw of the galvanometer, which was afterward reduced to ohms.

In the first series of observations, where the conductivity of end (1) of the crystal was measured there is a rather wide variation of the readings, but this was brought about by a deliberate variation of the lighting arrangement, extra screens to cut off stray light, etc., being used. The purpose was to make observations under corresponding conditions when each end was illuminated.

The result of these experiments can be stated as follows:

Both the direct and the transmitted actions are very rapid, more than 50 per cent. of the equilibrium change taking place in 0.4 second. In searching for an explanation of the fact that the percentage change of conductivity in 0.4 second was quite different depending on which end of the crystal was tested, facts were discovered which indicate that the ratio of the area illuminated to the cross sectional area conducting is a factor in the rate of change in short intervals of time. Whatever may be the outcome of a study of this relation, it is not believed that the accompanying results will be at all vitiated. Second, that the total amount of the transmitted action is of the same order of magnitude as the direct action and yet distinctly less. Third, the difference between

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[1] See Phys. Rev., Vol. 33, p. 403.

[2] Phys. Rev., Vol. 33, p. 53, 1911.

TABLE I.

Change of Resistance of Crystal at End (1).

	Illuminated at Electrode (2), Ohms.	Illuminated at (1), Ohms.
Resistance in dark	880,000	880,000
Resistance in equilibrium with light	450,000	370,000
Change of resistance at equilibrium	430,000	510,000
Change of resistance in 0.4 sec	7.0	9.0
	7.5	9.0
	7.0	11.5
	9.0	12.0
	9.0	12.5
	8.0	12.0
	7.5	12.0
	9.0	15.0
	11.0	15.0
	11.0	18.0
Mean in div	8.6	12.9
Mean ohms	183,000	234,000
Ratio, $\frac{\text{change in 0.4 sec.}}{\text{equilibrium change}}$	.426	.459

Change of Resistance Measured at End (2).

	Arranged to Illuminate end (1).	To Illuminate (2).
Resistance in dark	510,000	510,000
Resistance in equilibrium in light	340,000	260,000
Change of resistance at equilibrium	170,000	250,000
Change of resistance in 0.4 sec	11.0	18.0
	10.5	17.5
	11.0	16.5
	11.0	16.5
	10.0	14.5
Mean in div	10.7	16.6
Mean in ohms	136,000	215,000
Ratio, $\frac{\text{change in 0.4 sec.}}{\text{equilibrium change}}$	.80	.86
Change of resistance in 0.2 sec	10. div.	16.
	10.5	15.5
Mean in ohms	133,000	201,000
Ratio, $\frac{\text{change of resistance in 0.2 sec.}}{\text{equilibrium change}}$	.78	.80
Change of resistance in 0.1 sec	7.0 div.	13.5
	7.5	12.5
	7.5	12.5
Mean	7.3	12.8
In ohms	95,000	162,000
Ratio, $\frac{\text{change in 0.1 sec.}}{\text{equilibrium change}}$	.56	.65

the fractional parts of the total change taking place in 0.4 second for the direct and the transmitted effects is very small. The proportional change in 0.2 second is also observed to be the same within the limits of accuracy of the measurement. Even for 0.1 second exposure there is almost as great a fraction of the effect transmitted to the opposite end of the crystal as at the illuminated end.

The conclusion is fairly safe that practically all of the transmitted action by light may travel a distance of 2 mm. in less than 0.1 second. How much faster than 2 centimeters per second it may travel, I was not prepared to determine. At any rate the effect travels so fast that we are warranted in saying that it can not be transmission of a temperature change along the crystal. This conclusion is quite in agreement with recent experiments by Sieg and Brown,[1] in which it was shown that for equal quantities of energy in different parts of the spectrum falling on the crystal, a maximum transmitted effect occured in the visible spectrum, not far from the position where the maximum occurred for direct action of the light. Likewise, if the transmission is too rapid to be a transmitted temperature disturbance, it must, according to the electron theory, be too rapid to be merely an equalization of electronic pressures throughout the crystal.

The Action at a Distance is Propagated Mechanically.

The fundamental fact is that light falls on a crystal of selenium at one spot and produces a change of conductivity at any other part of the crystal. It is inconceivable that the light itself could, on entering a crystal, diffuse almost without absorption to the most distant part of a crystal, and yet such may be the case. Therefore the nature of this transmitted effect was investigated along other lines. One view would suppose the light by virtue of its electromagnetic properties to be able to directly tear the electrons free from the atomic structure. In order that there might be almost undiminished action at a distance, either these electrons must disperse to all parts of the crystal structure or at the place where the light falls there must be an increased concentration of electrons which would quickly be felt throughout the crystal, the same as an increased quantity of gas in one part of a tank system would be felt everywhere in the enclosure. The velocity of such a disturbance would be largely a function of the elastic properties of the electrons in confined space. Another view is that the light acts upon a certain mechanism which produces automatically a certain instability throughout the crystal structure. This instability manifests itself by a greater electrical con-

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[1] Phys. Rev., N. S., vol. 4, p. 507, 1914.

ductivity, which means either an increased number of free electrons or a greater instability of the fixed electrons. The first view involves the direct carrying over of the action without the aid of the crystal structure as such while the second view involves something analogous to an elastic medium propagation.

The merits of the above views were investigated largely with the use of the arrangement shown in Fig. 1. In my previous paper it was pointed out that the resistance of a crystal varies with the mechanical pressure under which it exists and also that the resistance varies with the potential differences producing the current. With this apparatus were studied the interaction of various agents, viz. light, pressure and electrical potentials, that alter the resistance of the crystal.

It was found, no matter how much the resistance might change at end (1) as a result of large differences of potential there, that the resistance at the opposite end (2) did not vary. Similarly pressure on end (1) of the crystal by the screw S_1 changed the resistance at (1) by a factor of ten but the resistance at the opposite end was thereby changed only by a zero or negligible amount. Thus we have the clear cut result that *light-action is transmitted along the crystal, but the pressure effects and the electrical potential effect*, as I have designated them, *are not transmitted.*

A most important part of the experiment was in the superposition of the pressure and the light effects. In this experiment only end (1) of the crystal was illuminated in all the observations. The conductivity was measured at both ends simultaneously, both when end (1) was in the dark and when it was illuminated. The observations are shown in Table II. The pressures were deduced from the conductivity values according to the relation found in an earlier paper.[1] The illumination was practically constant throughout. A brief study of the table will verify the following generalization: *the increase of pressure increases the light sensibility (i. e., the change of conductivity due to constant illumination) only when the pressure is applied to the part of the crystal where the conductivity is being measured.*

From the results stated we are warranted in making the following deductions: If electrical conduction in these crystals is due to *free electrons that exist in equilibrium according to the Maxwell-Boltzman law, it can not be possible that the mechanical pressure in increasing the conductivity increases the number of free electrons.* This follows because the pressure effect is not transmitted from one part of the crystal to another and because the light-sensitiveness with varying pressure remains constant everywhere except at the points where the pressure is applied. There might, of course,

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[1] PHYS. REV., Ser. 2, Vol. 4, p. 85, 1914.

TABLE II.

Conductivity of Lamellar Crystal, $\times 10^7$.

<table>
<tr><th></th><th>Between Electrodes at (1).</th><th>Between Electrodes at (2).</th></tr>
<tr><td>In dark</td><td>4.0, 4.0, 4.0</td><td>4.8, 4.5, 5.0</td></tr>
<tr><td>End (1) illuminated.</td><td>7,8, 8.0, 8.0</td><td>6.9, 7.4, 7.7</td></tr>
<tr><td>Increase of conductivity</td><td>3.8, 4.0, 4.0 mean 3.9 div.</td><td>2.1, 2.9, 2.7 mean 2.6 div.</td></tr>
<tr><td colspan="3">Pressure on (1) 3, kgm./cm^2. on (2) 2 kgm.
Pressure increased by S_1.</td></tr>
<tr><td>In dark</td><td>8.0, 8.8, 8.8</td><td>5.2, 5.3, 5.3</td></tr>
<tr><td>End (1) illuminated.</td><td>16.0, 16.6, 16.4</td><td>7.8, 7.8, 7.8</td></tr>
<tr><td>Increase</td><td>8.0, 7.8, 7.6 mean 7.8</td><td>2.6, 2.5, 2.5 mean 2.6</td></tr>
<tr><td colspan="3">Pressure on (1) 6, on (2) 2 kgm./cm^2.
Pressure increased by S_1.</td></tr>
<tr><td>In dark</td><td>28.0, 31.6, 31.6</td><td>5.3, 5.3, 5.4</td></tr>
<tr><td>End (1) illuminated.</td><td>52.8, 52.6, 52.2</td><td>7.3, 7.5, 7.2</td></tr>
<tr><td>Increase</td><td>24.8, 21.0, 20.6 mean 22.1</td><td>2.0, 2.2, 1.8 mean 2.0</td></tr>
<tr><td colspan="3">Pressure on (1) 18 kgm./cm^2., on (2) kgm./cm^2.
Pressure increased by S_2.</td></tr>
<tr><td>In dark</td><td>20.0, 24.0, 26.0, 25.6</td><td>20.0, 20.0, 25.0, 25.0</td></tr>
<tr><td>End (1) illuminated.</td><td>40.0, 42.0, 48.0, 47.0</td><td>23.2, 30.3, 33.0, 34.5</td></tr>
<tr><td>Increase</td><td>20.0, 18.0, 22.0, 21.0 mean 20.2</td><td>3.2, 7.3, 8.0, 9.5 mean 7.0</td></tr>
<tr><td colspan="3">Pressure on (1) 18 kgm./cm^2., on (2) 6 kgm./cm^2.
Pressure increased by S_2.</td></tr>
<tr><td>In dark</td><td>25.4, 26.0, 26.4</td><td>68.9, 71.4, 74.0</td></tr>
<tr><td>End (1) illuminated.</td><td>48.8, 48.6, 47.0</td><td>81.3, 86.9, 88.5</td></tr>
<tr><td>Increase</td><td>23.4, 22.0, 20.6 mean 22.0</td><td>12.4, 15.5, 14.5 mean 14.5</td></tr>
<tr><td colspan="3">Pressure on (1) 18 kgm./cm^2., on (2) 13 kgm./cm^2.</td></tr>
</table>

be a transmission of the pressure effect of secondary magnitude and importance which would not be detected except in more highly refined work. Then at least that part of the conduction that is brought about by increased pressures can not result from an increase in number of dynamically free electrons, and likewise that part of the increased conductivity that comes from a constant illumination as a result of increased pressure can not arise from free electrons at constant pressure everywhere within the crystal. Of course this argument requires that the increased pressure reacts against the fixed crystal structure and not against the free electrons. Now if the increased conductivity resulting from pressure on the crystal is not due to free electrons, it is difficult to justify conduction by free electrons at atmospheric pressure. The conclusion then seems unavoidable *that electrical conduction in crystals of metallic selenium can not be due to the traditional free electron.*

This conclusion need not be inconsistent with the result of Richardson and Brown[1] that the electrons inside a metal are free in the sense of the kinetic theory of gases, for our result was based upon work with highly conducting metals. Perhaps conduction in all non metals is like that in selenium crystals and dissimilar to that in the good conductors. It might be urged that the conductivity of selenium crystals is a function both of the number of free electrons and of a resisting medium through which they must pass. But this particular motion is inconsistent with the rapid transmission of the light-action along the crystal as was found.

The most satisfying unification of the experiments related that I have been able to conceive rests upon the hypothesis of conduction by electrons in semi-stable equilibrium. Scattered throughout the crystal structure are centers, perhaps atomic center, in which are associated charges of electricity in almost unstable equilibrium. Electrons free to move about in the structure as gas molecules move in enclosure do not exist. True these electrons are fixed in number and in position in the crystal structure, but the degree of their stability will vary with the agencies acting on the crystal. Electrical conduction consists essentially of a pulling out of these electrons from their moorings in the direction of the electrical stress. While out of position an electron might behave temporarily as a free electron in equilibrium with the heat and electrical forces about it. This process of conduction bears a little resemblance to the transfer of electricity in electrolytes.

The fact that Ohm's law does not hold for these crystals or metallic selenium generally is against the free electron hypothesis. The conductivity increases very greatly as the electrical forces in the line of conduction increase, until a saturation value of the conductivity is reached.

On this view increased pressure or tension on the selenium reduces the electrons to an average lower degree of stability. Thus a given fall of potential across the crystal will be able to dislocate a larger number of electrons from their fixed positions, or will be able to use them on an average a longer time before they recombine.

Similarly, light by some mechanism yet undiscovered lowers the degree of stability of the electrons throughout the crystal or further the mechanism controlled by light frees the most unstable electrons throughout the selenium. Thus as found if pressure is applied to any part of the crystal and any other part of the crystal is illuminated, that part of the

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[1] Phil. Mag. (6), Vol. 16, p. 353, 1908, and Phil. Mag. (6), Vol. 18, p. 649, 1909.

crystal under pressure, and only that part, has its absolute light-sensitiveness increased. This merely means that at the place of great pressure the mechanism of light finds a greater number of electrons in such a low degree of stability that more of them can be kept in the free state.

It is still to be investigated how the light-action may be transmitted to a distance. It has occurred to the writer that it may be a change of crystalline structure, or an elastic vibration, or merely light diffusion.

DETERMINATION OF Ne FOR HYDROGEN FROM MEASUREMENTS OF BROWNIAN MOVEMENTS.

By Carl F. Eyring.

Introduction.

VALUES of Ne for gaseous ionization have been determined by Townsend,[1] Franck and Westphal,[2] Fletcher, and others. By means of the measurement of the Brownian movements of a small oil drop, Fletcher[3] in 1911 made a direct determination of Ne for ionized air, and more recently[4] determined by the same method the value of the Avogadro constant N for air. Working with the same apparatus the writer attempted a determination of N for hydrogen, but obtained results which seem to indicate that the *ak* factor of the law of fall for hydrogen is different from that obtained by Millikan[5] for air. The determination of Ne was then undertaken since it does not involve the factor *ak*. The present article extends the Brownian movement method of Fletcher to the study of hydrogen with the view of testing the method in the case of gases other than air, and of determining directly the value of Ne for hydrogen.

§ I. Equations Used, Apparatus, and Method of Procedure.

The formula deduced by Fletcher[6] for the Avogadro constant N is

$$N = \frac{RTz^2}{6\pi\mu ak V_0^2 t_0}, \tag{1}$$

where R is the gas constant, T the absolute temperature, a the radius of the oil drop, μ the coefficient of viscosity of the gas through which it moves, t_0 its time of fall under gravity, V_0 its average velocity of fall, k a factor of the law of fall that depends on the radius of the drop and the mean free path of the gaseous molecules, and z a term, defined by equation (4) below, that comes from the solution of the integral that involves the Brownian movements of the oil drop.

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[1] Proc. Roy. Soc., A, Vol. LXXX., p. 209, 1908.

[2] Verh. D. Phys. Ges., Juli 2, 1909.

[3] Phys. Rev., Vol. XXXIII., No. 2, Aug., 1911.

[4] Phys. Rev., Vol. IV., s. series, No. 5, Nov., 1914.

[5] Phys. Rev., Vol. I., s. series, p. 219, 1913.

[6] Phys. Rev., Vol. IV., s. series, No. 5, p. 442, Nov., 1914.

The motion of a sphere of charge e in an electrostatic field of intensity X is determined by

$$Xe = 6\pi\mu ak\frac{V_1 + V_2}{2}, \tag{2}$$

where V_1 is the velocity of fall and V_2 the velocity of rise against gravity.

Combining equations (1) and (2), the equation used for the determination of Ne is

$$Ne = \frac{RTz^2}{V_g^2 t_g X} \cdot \frac{V_1 + V_2}{2}. \tag{3}$$

All the quantities of the right hand member of this equation can be measured by experiment.

The apparatus, consisting of the lighting system, the observing system, the timing system, and the vessel containing hydrogen and suspended oil drops, is that described in detail by Fletcher,[1] with the addition of a hydrogen generating system and a slightly modified arrangement for blowing the oil drops. The hydrogen was generated from good chemicals, and was passed through potassium permanganate solution to remove impurities, and concentrated sulphuric acid and calcium chloride to remove moisture. The vessel was filled with hydrogen to the desired pressure, and the oil drops were blown by hydrogen from the atomizer into the vessel and between the condenser plates. Every precaution was taken to keep air from the chamber.

The method used to determine the quantities given in equation (3) by use of this apparatus has been described in detail by Fletcher,[2] and consists first of observing the Brownian movements of a very small oil drop (liquid vaseline) as it falls under the influence of gravity between two uncharged condenser plates, and then of observing its time of fall and rise under an electrostatic field of known intensity. The drop responds to the electric field when it contains one or more charges which it has caught from the ionized hydrogen. The ionization is produced by X-rays.

A scale of fifty divisions of known length is mounted in the eye piece of the observing telescope, and in observing the Brownian movements, the time is recorded as the drop crosses each division. When the full scale has been covered, the drop is raised by means of the electrostatic field, and observations are again taken. By a repetition of this process, as many as 1,666 observations were taken for a single drop (Table III., below). The average of all these times of fall is taken as t_g, and V_g is obtained from t_g and the length of the scale division b. The factor z of equation (3) is defined by the equation

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[1] *L. c.*, p. 443.

[2] *L. c.*, p. 446.

$$z = \frac{2t_g}{\sqrt{\pi\tau}}\left(1 + \frac{1}{2z^2} + \frac{1}{4z^4} + \frac{3}{8z^6} + \cdots\right), \tag{4}$$

where

$$\tau = \frac{\overset{+}{t}_a - \overset{-}{t}_a}{2},$$

$\overset{+}{t}_a$ being the average of all times of fall greater than t_g, and $\overset{-}{t}_a$ being the average of all times of fall less than t_g.[1] The factor z which thus involves the Brownian movements of the oil drop, can be calculated to any desired degree of accuracy from equation (4).

The gas constant R is taken as 83.15×10^6. The electrostatic field X is determined by finding the difference of potential between the condenser plates by a Kelvin multicellular electrometer. The plate distance is 1.605 cm.

§ II. THE DATA.

The tables contain the average values which were computed from the observations on seven drops. Over 10,000 observations of the Brownian movements were made under good experimental conditions. Part I. of the tables contains the velocities of the drop in the electrostatic field. The quantities V_1', V_1'', V_1''', $\cdots$; V_2', V_2'', V_2''', $\cdots$ are the velocities of fall and rise respectively in the electrostatic field when the drop has 1, 2, 3, etc., charges. The values $V_1^{(n)} + V_2^{(n)}$, from which n is clearly determined, are divided by n to reduce to the condition of a single charge, and the average of all such values is used in equation (3). In Part II. of the tables, column 1 gives the constant distance over which time of fall under gravity was taken, column 8 gives the value of Ne calculated from equation 3, column 9 gives the number of observations, and the other columns give the average values computed from the Brownian movements of the drop.

TABLE I.

Drop 1.

Temperature 21.1° *C.* *Pressure* 30.12 *cm.*

Part I.

Volts = 993.1. $V_1' = .0378$. $V_1' + V_2' = .0678$ per charge.

$X = 2.062$. $V_2' = .0300$.

Part II.

b	t_g	V_g	t_a	$\overset{-}{t}_a$	τ	z	Ne	No. Obs.
.00922	2.079	.00444	2.552	1.693	.429	5.46	2.99×10^{14}	235
.01844	4.158	.00444	4.785	3.529	.628	7.46	2.79×10^{14}	167

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[1] See Fletcher, *l. c.*, p. 441, for the values of $\overset{+}{t}_a$ and $\overset{-}{t}_a$ as deduced from the Brownian movement theory.

TABLE II.

Drop 2.

Temperature 20.8° *C.* *Pressure* 30.39 *cm.*

Part I.

Volts = 290.6. $V_1'' = .0232.$ $V_1'' + V_2'' = .0361.$

$X = .604.$ $V_2'' = .0129.$ $\therefore V_1' + V_2' = .0180$ per charge

Part II.

b	t_g	V_g	$\overset{+}{t_a}$	$\overset{-}{t_a}$	τ	z	Ne	No. Obs.
.00922	1.863	.00495	2.220	1.531	.344	6.18	3.05x10^{14}	1019
.01844	3.724	.00495	4.240	3.284	.478	8.83	3.08x10^{14}	509
.02766	5.586	.00495	6.196	5.011	.592	10.70	3.05x10^{14}	337
.03688	7.448	.00495	8.191	6.790	.700	12.04	2.91x10^{14}	254

TABLE III.

Drop 3.

Temperature 20.5° *C.* *Pressure* 16.41 *cm.*

Part I.

Volts = 1,414.7. $V_1'' = .0832.$ $V_1' = .0449.$

$X = 2.938.$ $V_2'' = .0718.$ $V_2' = .0329.$

$V_1'' + V_2'' = .1551.$ $V_1' + V_2' = .0778.$

$\therefore V_1' + V_2' = .0777$ per charge.

Part II.

b	t_g	V_g	$\overset{+}{t_a}$	$\overset{-}{t_a}$	τ	z	Ne	No. Obs.
.0118	1.963	.00601	2.254	1.672	.278	8.04	2.94x10^{14}	1666
.0236	3.926	.00601	4.370	3.542	.414	10.78	2.65x10^{14}	831
.0354	5.889	.00601	6.372	5.393	.489	13.66	2.84x10^{14}	550
.0472	7.852	.00601	8.389	7.277	.556	16.00	2.92x10^{14}	410
.0590	9.815	.00601	10.479	9.227	.626	17.85	2.91x10^{14}	315

TABLE IV.

Drop 4.

Temperature 21.0° *C.* *Pressure* 52.39 *cm.*

Part I.

Volts = 1,074.1. $V_1' = .0165.$ $V_1'' = .0308.$ $V_1''' = .0447.$

$X = 1.233.$ $V_2' = .0113.$ $V_2'' = .0251.$ $V_2''' = .0396.$

$V_1' + V_2' = .0278.$ $V_1'' + V_2'' = .0559.$ $V_1''' + V_2''' = .0843.$

$V_1^{IV} = .0575.$

$V_2^{IV} = .0527.$

$V_1^{IV} + V_2^{IV} = .1102.$

$V_1' + V_2' = .0278$ av. per charge.

Part II.

b	t_g	V_g	$\overset{+}{t_a}$	$\overset{-}{t_a}$	τ	z	Ne	No. Obs.
.00937	3.640	.00254	4.320	3.069	.625	6.65	2.87x10^{14}	846
.01874	7.280	.00254	8.180	6.477	.851	9.85	3.15x10^{14}	421
.02811	10.920	.00254	12.024	9.913	1.055	11.75	2.99x10^{14}	278

TABLE V.

Drop 5.

Temperature 21.2° *C.* *Pressure* 52.78 *cm.*

Part I.

Volts = 1,044.8. $V_1{}' = .0138.$ $V_1{}''' = .0337.$ $V_1{}^{IV} = .0422.$
$X = 2.170.$ $V_2{}' = .0060.$ $V_2{}''' = .0257.$ $V_2{}^{IV} = .0346.$
$V_1{}' + V_2{}' = .0198.$ $V_1{}''' + V_2{}''' = .0594.$ $V_1{}^{IV} + V_2{}^{IV} = .0768.$
$V_1{}^{V} = .0537.$ $V_1{}^{VII} = .0734.$
$V_2{}^{V} = .0462.$ $V_2{}^{VII} = .0651.$
$V_1{}^{V} + V_2{}^{V} = .0999.$ $V_1{}^{VII} + V_2{}^{VII} = .1385.$
$V_1{}' + V_2{}' = .0198$ av. per charge.

Part II.

b	t_g	V_g	$\overset{+}{t_a}$	$\overset{-}{t_a}$	τ	z	Ne	No. Obs.
.01874	4.770	.00393	5.198	4.335	.431	12.54	2.39×10^{14}	551
.03748	9.540	.00393	10.068	8.993	.537	19.90	3.01×10^{14}	276
.05622	14.310	.00393	15.076	13.631	.722	22.40	2.54×10^{14}	178

TABLE VI.

Drop 6.

Temperature 20.8° *C.* *Pressure* 55.30 *cm.*

Part I.

Volts = 1,118.1. $V_1{}' = .0243.$ $V_1{}'' = .0440.$ $V_1{}''' = .0625.$
$X = 2.320.$ $V_2{}' = .0140.$ $V_2{}'' = .0337.$ $V_2{}''' = .0526.$
$V_1{}' + V_2{}' = .0383.$ $V_1{}'' + V_2{}'' = .0777.$ $V_1{}''' + V_2{}''' = .1153.$

$\therefore\ V_1{}' + V_2{}' = .0385$ av. per charge, and $\dfrac{V_1{}' + V_2{}'}{X} = .0166.$

Volts = 1,123.8. $V_1{}' = .0233.$ $V_1{}'' = .0426.$ $V_1{}''' = .0611.$
$X = 2.338.$ $V_2{}' = .0154.$ $V_2{}'' = .0345.$ $V_2{}''' = .0543.$
$V_1{}' + V_2{}' = .0387.$ $V_1{}'' + V_2{}'' = .0781.$ $V_1{}''' + V_2{}''' = .1154.$

$\therefore\ V_1{}' + V_2{}' = .0388$ av. per charge and $\dfrac{V_1 + V_2}{X} = .0166.$

$$\therefore\ \frac{V_1 + V_2}{X} = .0166 \text{ av.}$$

Part II.

b	t_g	V_g	$\overset{+}{t_a}$	$\overset{-}{t_a}$	τ	z	Ne	No. Obs.
.01674	4.679	.0040	5.191	4.155	.518	10.27	2.83×10^{14}	446
.03748	9.358	.0040	10.145	8.667	.739	14.33	2.75×10^{14}	221

TABLE VII.

Drop 7.

Temperature 20.8° *C.* *Pressure* 55.30 *cm.*

Part I.

Volts = 1,123.8. $V_1{}' = .0233.$ $V_1{}'' = .0426.$ $V_1{}''' = .0611.$
$X = 2.338.$ $V_2{}' = .0154.$ $V_2{}'' = .0345.$ $V_2{}''' = .0543.$
$V_1{}' + V_2{}' = .0387.$ $V_1{}'' + V_2{}'' = .0781.$ $V_1{}''' + V_2{}''' = .1154.$

$V_1{}' + V_2{}' = .0388$ av. per charge. $\dfrac{V_1{}' + V_2{}'}{X} = .0166.$

Volts = 1,121.4. $V_1'' = .0421.$ $V_1'' + V_2'' = .0773.$

$X = 2.330.$ $V_2'' = .0352.$ $V_1' + V_2' = .0386$ per charge.

$$\frac{V_1 + V_2}{X} = .01658. \quad \therefore \quad \frac{V_1 + V_2}{X} = .01659 \text{ av.}$$

Part II.

b	t_g	V_g	$\overset{+}{t_a}$	$\overset{-}{t_a}$	τ	z	Ne	No. Obs.
.01874	5.143	.00365	5.762	4.570	.596	9.78	2.83×10^{14}	379
.03748	10.286	.00365	11.156	9.475	.840	13.88	2.85×10^{14}	188

TABLE VIII.

A Summary of the Values of Ne and the Corresponding Number of Observations.

Drop.	Ne + 10^{14}	No. of Obs.	Drop.	Ne + 10^{14}	No. of Obs.
1	2.99	235		2.87	846
	2.77	167	4	3.15	421
				2.99	278
	3.05	1019			
2	3.08	509		2.39	551
	3.05	337	5	3.01	276
	2.91	254		2.54	178
	2.94	1666	6	2.83	446
	2.65	831		2.75	221
3	2.84	550			
	2.92	410	7	2.83	379
	2.91	315		2.85	188

Assigning weights to the values of Ne according to the number of observations, the average value

$$Ne = 2.880 \times 10^{14}$$

is obtained. The value of Ne obtained from electrolysis is 2.896×10^{14}. The average value differs from this by .5 per cent.

The results of this investigation lead, therefore, to the conclusion that the Brownian movement method holds for gases other than air, and that the molecules of ionized hydrogen carry the same charge as the hydrogen ions of electrolysis.

This investigation was made in the Physical Laboratory of the Brigham Young University on the suggestion and with the generous assistance of Professor H. Fletcher.

FLUORESCENCE OF THE URANYL SALTS UNDER X-RAY EXCITATION.

BY FRANCES G. WICK.

THE fluorescence spectrum characteristic of the uranyl salts is known to consist of several narrow bands, sometimes as many as seven, regularly arranged and sharply defined. An extended study of these salts has recently been made by Nichols and Merritt[1] with a view to discovering whether the fluorescence bands in a given salt are independent of each other, or whether they form a series so connected that any agency which excites one of the bands excites the others also. In this investigation, light of different wave-lengths was used for excitation and the fluorescence, in each case, was carefully observed to determine whether or not certain regions of the spectrum might excite the bands independently of each other.

A variation of the form of the fluorescence curve was found with different exciting lights. This, however, was explained by the fact that the absorption of both the exciting light and the fluorescent light varies with wave-length. The fluorescence bands for which the absorption is greatest appear weaker when the exciting light penetrates to a great distance in the salt than when it is absorbed by a comparatively thin surface layer. The conclusion reached by Nichols and Merritt is that for a layer of the salt so thin that absorption would be negligible, the form of the fluorescence spectrum would be the same for all excitations and the observed distribution of energy would correspond to the actual distribution. The fluorescence of these salts appears to be due to vibrations set up in a single connected mechanism and any agency which excites one of the bands in a given salt excites the others also.

It seemed of interest, in this connection, to determine whether or not the spectra of the fluorescence excited by X-rays differed in any way from that excited by other sources. With this end in view, a series of experiments was undertaken, at the suggestion of Professors Nichols and Merritt, upon some uranyl salts freshly prepared for them. Most of these salts could be excited to fluorescence in varying degrees of intensity by the violet light of the carbon arc.

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[1] Nichols and Merritt, PHYS. REV., Vol. 33, p. 354, 1911.

In order to determine which of the specimens were excited to fluorescence by X-rays, a preliminary test was made, the source of excitation being X-rays from a water-cooled tube with a parallel spark gap of from five to eight inches. The tube was run by current from an induction coil, to the primary of which was connected a mercury interrupter, no attempt being made to keep the current and voltage constant.

The intensity of the fluorescence excited in the different salts varied greatly, being, in every case, much less than that excited by the violet light of the arc. The salts under observation were roughly divided into three groups with respect to the brightness of the fluorescence excited. These groups are as follows:

Group 1.

Salts in which the Fluorescence is Relatively Bright.

Uranyl cæsium sulphate.
Uranyl potassium sulphate.
Uranyl rubidium sulphate.
Uranyl sodium sulphate.
Uranyl potassium nitrate.

Group 2.

Salts in which the Fluorescence is Faint.

Uranyl acetate.
Uranyl ammonium acetate.
Uranyl ammonium chloride.
Uranyl nitrate.
Uranyl nitrate tri-hydrate.

Group 3.

Salts which were not Excited to Fluorescence.

Uranyl acetate.
Uranyl ammonium fluoride.
Uranyl antimony tartarate.
Uranium fluoride.
Uranyl iodate.
Uranyl oxalate.
Uranyl potassium fluoride.
Uranyl tartarate.
Uranyl potassium tartarate.
Uranyl thallous sulphate.

The same salts were later exposed to X-rays from a Coolidge tube running at high voltage and current. The fluorescence of the first two groups was greatly increased and the third group all showed some fluorescence except the following:

Uranyl antimony tartarate.
Uranium fluoride.
Uranyl potassium tartarate.
Uranyl thallous sulphate.

These salts showed no fluorescence under excitation by light. The variation in the intensity of the other salts under light and X-ray excitation seemed to follow approximately the same order.

In order to determine whether the fluorescence excited by X-rays differed, in any way, from that excited by the violet light of the arc, a comparison of the spectra of the fluorescence excited by the two sources was made. The apparatus was arranged as shown in Fig. 1. A thin layer of the salt to be observed was mounted between two glass plates and placed at *S*, a short distance in front of the collimator slit *C*, of a spectrometer. X-rays from a water-cooled tube, *T*, were allowed to pass through the specimen, the fluorescence being observed from the side of emergence of the X-rays. The rays were so penetrating that the fluorescence of the incident and emergent sides of the specimen did not differ perceptibly. A heavy lead screen, *L*, was used for protection. A right-angled arc, *A*, was set up in such a way that the light from the arc, after passing through a converging lens, *E*, and a heavy blue glass, *D*, could be thrown obliquely on the specimen, *S*, without changing any of the adjustments.

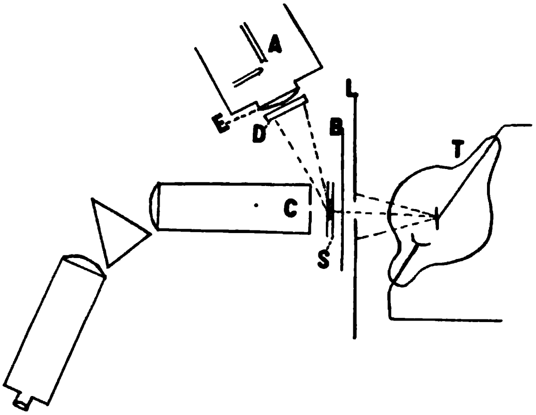

Fig. 1.

The first salt to be examined in this way was uranyl cæsium sulphate. The spectrum of the fluorescence excited by the arc consisted of six bands which could be easily observed. The bands toward the violet end of the spectrum, *a*, *b*, *c*, and *d* were bright, each having a sharply defined crest, the intensity fading off gradually toward the longer wave-lengths, and more abruptly toward the shorter wave-lengths—the usual form of the fluorescence bands. The red bands, *e* and *f*, were broad and dim without any well-defined crest.

Excitation of this salt by X-rays produced fluorescence of such low intensity that it was necessary for the observer to be in absolute darkness for some time before attempting to make any settings. The difficulty of making observations was increased by the fact that it was possible to run the X-ray tube with safety for only short intervals of time. Bands *a*, *b*, *c*, and *d*, were similar to the corresponding bands excited by light, the only difference observable being one of brightness. Bands *e* and *f* which were broad and dim under light excitation, did not appear under excitation by X-rays.

Fluorescence Bands of Uranyl Salts.

	Wave-length of Bands.					
	a	*b*	*c*	*d*	*e*	*f*
Uranyl cæsium sulphate.						
Light excitation.......	4866	5080	5320	5560	5860	6190
X-ray excitation......	4863	5073	5325	5565	....	....
Uranyl potassium sulphate.						
Light excitation.......	4918	5137	5385	5610	5900	6228
X-ray excitation......	4908	5132	5388	5615	....	....
Uranyl rubidium sulphate.						
Light excitation.......	4915	5140	5380	5613	5910	
X-ray excitation......	4920	5135	5378	....	....	
Uranyl sodium sulphate.						
Light excitation.......	4910	5114	5375	5605	5903	
X-ray excitation......	4915	5118	5378	....	....	
Uranyl potassium nitrate.						
Light excitation.......	4870	5096	5332	5595	5890	6197
X-ray excitation......	4865	5110	5337	5590	....	....
Uranyl nitrate tri-hydrate.						
Light excitation	4880	5098	5350	5610	5905	6275
X-ray excitation......	4861	5100	5370	....	....	....

The results of measurements of the wave-lengths of the crests of these bands under the two sources of excitation are shown in the accompanying table. The wave-lengths of the crests of the corresponding bands are found to be the same within the limits of observational errors. The difference is not so great as that between the individual settings upon the same crest. Because of the low intensity of the fluorescence under X-rays, it was necessary to have the collimator slit wider open than is desirable for accurate determination of wave-length. In each case, several settings were made and the wave-length corresponding to the average determined from a calibration curve.

As a check upon these results, the indicator in the eyepiece of the spectrometer was repeatedly set upon the crest of one of the bands excited by one source, then the excitation was changed, without changing any of the adjustments, and the indicator was found to have exactly the same position with reference to the band.

Measurements of this kind were made upon all the salts given in the table. The only difference which could be detected in the position and character of the bands when the source of excitation was changed, was such as might have been due to a change in intensity of fluorescence. In every case, the intensity of the bands was less and the number of bands observed fewer under X-ray excitation. The bands which were missing were those in the red end of the spectrum which were comparatively broad and dim under excitation by light.

These results are in agreement with the conclusions reached by Nichols and Merritt that the fluorescence of the salts is due to a mechanism the parts of which are so related that any source which excites one of the bands excites the others, also.

An attempt was made to photograph the fluorescence spectra excited by more powerful X-rays from a Coolidge tube running at a voltage of 45 kilovolts and a current of 30 milli-amperes. An exposure amounting to 30 minutes made by a series of excitations of from 30 to 45 seconds duration with sufficient time between to allow the target to cool, produced no satisfactory results.

Later experiments showed that the intensity of fluorescence was greatly increased by raising the voltage of the tube but the safe time of running the tube was shorter. Further attempts at photographing the spectrum did not seem feasible.

PHOSPHORESCENCE OF THE URANYL SALTS AT LOW TEMPERATURES.

In order to make some observations upon the fluorescence of uranyl potassium sulphate at low temperatures, the specimen was placed in a glass tube and lowered into an unsilvered Dewar bulb containing liquid air. At this temperature, under the excitation of the violet light of the arc, the bands of the fluorescence spectrum showed the characteristic resolution into narrower bands.[1] This change could not be observed under X-ray excitation, probably because of the low intensity of the fluorescence.

At the low temperature acquired, the salt became phosphorescent, the effect being much brighter and of longer duration when X-rays were used for excitation than when the violet light of the arc was used at the same temperature. The salt is not perceptibly phosphorescent at room temperature.

The decay of the phosphorescence was at first very rapid, then much slower. Some observations were made to determine the general shape of the decay curve.

The apparatus was set up as shown in Fig. 2.

A specimen of uranyl potassium sulphate, *S*, was placed in a test-tube surrounded by liquid air in an unsilvered Dewar bulb, *D*, and the X-rays from a Coolidge tube, *C*, were allowed to strike it. For measurement of the intensity of the phosphorescence, a Weber photometer, *W*, was used, the comparison source being a low candle-power tungsten lamp, *L*. A thick lead screen, *A*, was used for protection.

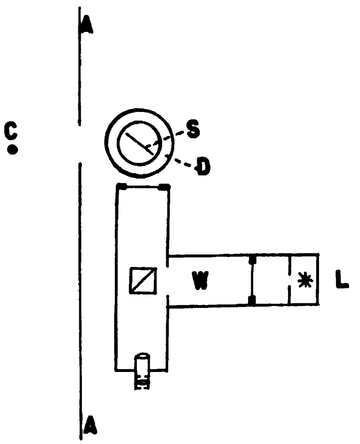

Fig. 2.

To produce phosphorescence, the specimen was exposed to the X-rays for two seconds, the time being accurately measured by a device attached to the apparatus for use in X-ray photography. The tube was running at 60 kilo-volts and 11.8 milli-amperes. A setting of the photometer was made when the specimen was under excitation, then the comparison field was cut down to a definite intensity and the time necessary for the phosphorescence to be reduced to this value was measured by means of a stop watch. The time was taken, in this way, for reduction to a number of different intensities. The decay curve obtained is shown in Fig. 3.

The decay was, at first, very rapid, then very slow, as is indicated by the shape of the curve. The faintness of the phosphorescence after the first very rapid decay, made it seem unwise to attempt to pursue this study with more refined apparatus for the measurement of time.

A number of the other uranyl salts were found to show this same

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[1] Nichols and Merritt, Phys. Rev., Vol. 33, p. 372, 1911.

peculiarity at the temperature of liquid air: under excitation of violet light, they were brilliantly fluorescent but showed little phosphorescence; under excitation by X-rays, the fluorescence was comparatively faint but the phosphorescence was much more pronounced.

The fact that the salts are so much more phosphorescent under excitation by X-rays than by light may be explained by a difference in absorption. When radiations from the exciting source were thrown normally upon a thin specimen of one of the salts, the fluorescence on the side of incidence was much more intense than on the side of emergence for excitation by light, but there was no perceptible difference in the intensity of the two sides with X-rays as the source of excitation.

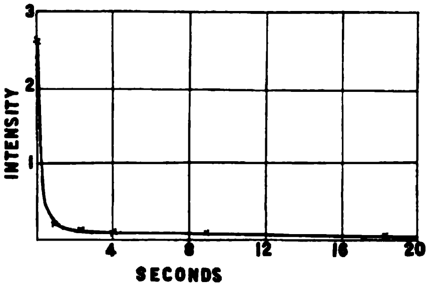

Fig. 3.

Decay of phosphorescence of uranyl-potassium sulphate after a two-second exposure to X-rays from a Coolidge tube.

Nichols and Merritt[1] found that the phosphorescence excited in Sidot Blende by cathode rays is less intense and more fleeting than that excited in the same substance under light excitation. This was accounted for by a difference in the penetration of the rays, light rays being more penetrating than cathode rays. The excitation by light is confined to a thin surface layer; under the more penetrating light rays the effect extends to a greater depth, resulting in a more gradual decay.

This explanation suggested the idea that the X-rays being more penetrating to the uranyl salts than light, the effect produced by them is deeper and lasts longer.

CONCLUSIONS.

The conclusions which may be drawn from the experiments described in this paper are as follows:

1. The fluorescence excited in the uranyl salts by X-rays differs from that excited by light in intensity only. The greater absorption of these salts for light than for X-rays accounts for the difference in intensity of fluorescence under the two sources.

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[1] Nichols and Merritt, PHYS. REV., Vol. 27, p. 349, 1908.

2. The phosphorescence following excitation by light is less intense and of shorter duration than that excited by X-rays. The difference in penetration of the two kinds of radiation seems to explain this, the more penetrating X-rays producing a phosphorescence which is more intense and of longer duration than that following the less penetrating light rays.

These experiments were carried on at Cornell University and I wish to express my sincere thanks to Professors Nichols, Merritt and Shearer for their interest and help and for their kindness in putting at my disposal the facilities of the laboratory.

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INTEGRATION OF THERMODYNAMIC EQUATIONS FOR AN IMPERFECT GAS.

BY SANFORD A. MOSS.

THE two laws of thermodynamics give certain differential equations connecting the heat-capacities of a substance with its pressure-volume relations, which have been integrated in special cases. A general integration is here made.

Total Heat.—The mathematical work is most readily accomplished by the use of " total heat," H, as the principal dependent variable. This is defined as the number of heat units added per unit of flow when a stream of fluid passes from a standard region to a region at a given pressure and temperature. It includes intrinsic or internal energy change due to molecular heat storage, dU, plus energy which has been supplied but which has not been added to the fluid in question. This latter represents work necessarily performed on the external universe, first, due to direct expansion $Apdv$, and second, required to force the fluid into the given region and out of the standard region, $Avdp$. (The sum of the first two terms is heat added to fluid in a closed envelope without flow, dQ, and we have $dH = dQ + Avdp$.) Now

$$vdp + pdv = d(pv)$$

so that

$$dH = dU + Ad(pv).$$

Since both terms on the right are exact functions, it follows that total heat is an exact function which has a fixed value for each condition, defined for instance by values of p and T, regardless of the manner in which the condition was reached. (This is really a form of statement of the First Law of Thermodynamics.) Total heat leads to simpler mathematical work than Q, which is not an exact function. It is in very general use by engineers. We will obtain general expressions for total heat for the gaseous state and for the liquid state, in terms of pressure and temperature. Then substitution of saturation pressure and temperature gives total heat for saturated vapor and saturated liquid. The difference between these two is latent heat of vaporization.

Notation and Definitions.—Quantities of heat, energy, total heat, etc., in heat units such as B.T.U. (pound-degree Fahrenheit) or calories (kilogram-degree Centigrade). Pressures in pounds per square foot or kilograms per square centimeter. Volumes in cubic feet or cubic centimeters.

A = reciprocal of mechanical equivalent of heat.

T = absolute temperature.

p = absolute pressure.

H = total heat as already explained. The change in H is heat added per unit weight when a substance flows from a point at one pressure and temperature to a point at another pressure and temperature. We arbitrarily take H as measured above liquid at p_0 and T_0, where T_0 is the triple point of water (freezing point at saturation pressure) which is practically 273.1° C. or 459.6° F., and p_0 is the saturation pressure of the substance being considered, at this arbitrary temperature.

U = internal or intrinsic energy measured above same point as H. Having defined H as an observed quantity as above we may define U by the relation $dH = dU + Ad(pv)$. We may take the first law of thermodynamics as being "U is an exact function," whence H is exact also, so that we can integrate directly, giving $H = U + Apv - Ap_0v_0$. Beyond we deduce various values of H, and values of U may be obtained from them by deducting $Apv - Ap_0v_0$. U is therefore given no further attention.

Q = heat added to unit weight when at rest in a closed envelope. From the above aspect of the first law of thermodynamics as well as the laws of hydrodynamics, it follows that $dH = dQ + Avdp$ and $dQ = dU + Apdv$.

ϕ = entropy, measured above same point as H. It is defined by the relation $d\phi = dQ/T$. The second law of thermodynamics may be taken as being "ϕ is an exact function." We have $dH = Td\phi + Avdp$ and $Td\phi = dU + Apdv$.

c_p = specific heat at constant pressure, defined as being $(dQ/dT)_p$ as well as $(dH/dT)_p$.

c_{p0} = value of c_p approached as pressure approaches 0. In general c_{p0} is a function of T.

c_v = specific heat at constant volume, defined as being $(dQ/dT)_v$. It follows

$$\left(\frac{dH}{dT}\right)_v = c_v + Av\left(\frac{dp}{dT}\right)_v.$$

The relations deduced throughout, unless specifically excepted, apply to either gaseous or liquid state. Where distinction between the two states is necessary, $vHU\phi c_p c_{p0} c_v$ will refer to gaseous state and $v'H'U'\phi' c_p' c_v'$ will refer to the liquid state. c_p' will be specific heat of liquid at the reference pressure p_0. In general c_p' is a function of T. Many of the relations also apply to the solid state, and when vH, etc., and $v'H'$, etc., appear, the relations may apply to gaseous and solid states. However this extension to solid state will not be definitely worked out.

μ = Joule-Thomson coefficient, defined as being $(dT/dp)_H$. From the general relation

$$\left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dT}\right)_H \left(\frac{dT}{dH}\right)_p = -1$$

it follows that

$$\left(\frac{dH}{dp}\right)_T = -\mu c_p.$$

q = total heat of saturated liquid, that is, value of H' for saturation values of p and T. We will consider this as true total heat, and for exactness will include a small volume term, usually ignored. True total heat of liquid for any values of p and T, not necessarily saturation, can be expressed just as is total heat of gas beyond, giving

$$H' = \int_{T_0}^{T} c_p' dT - AT^2 \int_{p_0}^{p} \left(\frac{d\{v'/T\}}{dT}\right)_p dp_T.$$

The last term can be written

$$-AT \int_{p_0}^{p} \left(\frac{dv'}{dT}\right)_p dp_T + A \int_{p_0}^{p} v' dp_T.$$

Here c_p' is the specific heat of liquid as a function of T for $p = p_0$. If p and T have saturation values the above expression becomes the general value for q. Or if c_p' and v' and the variation are along the saturation curve we have a similar expression. With no error (except near the critical point) the liquid volume v' may be taken constant so that we have as an approximate general expression for total heat of liquid in general,

$$H' = \int_{T_0}^{T} c_p' dT + Av'(p - p_0).$$

Here c_p' is the specific heat of liquid as a function of T, which must be independent of pressure when v' is constant (according to (7) beyond). If p and T have saturation values the last expression becomes a closely approximate value of q. That is

$$q = \int_{T_0}^{T} c_p' dT + Av'(p - p_0)$$

where p and T are saturation values.

We will not make the further common approximation of omitting the small term $Av'(p - p_0)$. This is usually done in steam tables without good reason. Omission of the term in steam turbine and engine computation gives energy of turbine minus energy of boiler feed pump. The complete expression for q gives energy of the turbine without this deduction. Total heat of saturated steam is often loosely defined as $r + \int_{T_0}^{T} c_p' dT$, which gives a value slightly different from total heat of superheated steam on the saturation line. This is avoided by the above definition of q.

n = entropy of saturated liquid, that is, value of ϕ' for saturation values of p and T. Entropy of liquid for any values, not necessarily saturation, as shown beyond for gases, is

$$\phi' = -A \int_{p_0}^{p} \left(\frac{dv'}{dT}\right)_p dp_T + \int_{T_0}^{T} \frac{c_p'}{T} dT,$$

where c_p' is specific heat of liquid as a function of T for $p = p_0$. If, however, p and T have saturation values, this becomes the the general expression for n. Or if c_p' and v' and the variation are along the saturation curve we have a similar expression. As in the case of q, we can take v' as constant (except near the critical point). Then entropy of the liquid is independent of pressure, and for any temperature entropy of saturated liquid is the same as entropy of liquid for all pressures. We have therefore as a closely approximate expression

$$n = \phi' = \int_{T_0}^{T} \frac{c_p'}{T} dT.$$

This is the expression usual in steam tables.

r = latent heat of evaporation. Value of $H - H'$ or $H - q$ for saturation values of p and T.

r_0 = value of r at p_0 and T_0.

λ = total heat of saturated steam or value of H for saturation conditions. $\lambda = q + r$.

u = volume increase at evaporation. Value of $v - v'$ for saturation values of p and T.

$f(T)$ = expression giving pressure of saturated vapor at temperature T. That is, the vapor pressure equation is $p = f(T)$.

$f'(T)$ = derivative of $f(T)$ with respect to T or value of dp/dT where p is saturation pressure.

Fundamental Differential Equations.—We will list some well-known relations which are the basis of our discussion. From the definition of ϕ and H

$$d\phi = \frac{1}{T}dH - A\frac{v}{T}dp.$$

By dividing by dT and putting p constant

$$\left(\frac{d\phi}{dT}\right)_p = \frac{c_p}{T}. \tag{1}$$

By dividing by dp and putting T constant

$$\left(\frac{d\phi}{dp}\right)_T = \frac{1}{T}\left(\frac{dH}{dp}\right)_T - A\frac{v}{T}. \tag{2}$$

By differentiating (1) and (2) we obtain values for $d^2\phi/dpdT$ which we can equate since ϕ is exact, yielding (after cancelling values of $d^2H/dpdT$ since H is exact)

$$\left(\frac{dH}{dp}\right)_T = Av - AT\left(\frac{dv}{dT}\right)_p. \tag{3}$$

An equivalent expression is

$$\left(\frac{dH}{dp}\right)_T = -AT^2\left(\frac{d\{v/T\}}{dT}\right)_p. \tag{4}$$

This is our fundamental relation between heat contents and volume. We later integrate it so as to obtain both v in terms of H and H in terms of v.

An auxiliary relation is found by multiplying each side of (3) by $(dp/dv)_T$,

$$\left(\frac{dH}{dv}\right)_T = Av\left(\frac{dp}{dv}\right)_T + AT\left(\frac{dp}{dT}\right)_v. \tag{5}$$

A special case of this equation is the well-known Clapeyron equation for a body of wet vapor,

$$\frac{r}{u} = ATf'(T). \tag{6}$$

By differentiation of (3) with respect to T, with p constant

$$\left(\frac{dc_p}{dp}\right)_T = -AT\left(\frac{d^2v}{dT^2}\right)_p. \tag{7}$$

This has been called the "Clausius relation." From (2) and (3) we have a general relation giving entropy in terms of volume

$$\left(\frac{d\phi}{dp}\right)_T = -A\left(\frac{dv}{dT}\right)_p. \tag{8}$$

By differentiation of (5) with respect to T with v constant

$$\left(\frac{dc_v}{dv}\right)_T = AT\left(\frac{d^2p}{dT^2}\right)_v.$$

c_v might be obtained by integration of this equation in the same way as we later obtain c_p from (7). However it will usually be more convenient to first obtain c_p and then obtain c_v from a relation which we deduce by combining

$$\left(\frac{dH}{dT}\right)_v = c_v + Av\left(\frac{dp}{dT}\right)_v$$

and

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dH}{dT}\right)_v + \left(\frac{dH}{dv}\right)_T\left(\frac{dv}{dT}\right)_p$$

with (5), which gives

$$c_v = c_p - AT\left(\frac{dp}{dT}\right)_v\left(\frac{dv}{dT}\right)_p$$

$$= c_p + AT\left(\frac{dv}{dT}\right)_p^2\bigg/\left(\frac{dv}{dp}\right)_T.$$

Beyond we deduce various values of c_p and values of c_v may be obtained from them by use of this expression. c_v is therefore given no further consideration.

The Joule-Thomson coefficient μ may also be obtained from the value of c_p by use of the relation

$$(dH/dp)_T = -\mu c_p$$

and (3) which gives

$$\mu = -\frac{Av - AT\left(\dfrac{dv}{dT}\right)_p}{c_p} = \frac{AT^2\left(\dfrac{d\{v/T\}}{dT}\right)_p}{c_p}.$$

μ is therefore given no further consideration.

We have as a general relation

$$dH = c_p dT + \left(\frac{dH}{dp}\right)_T dp.$$

If we substitute for $(dH/dp)_T$ from (3) and also stipulate that the variation of H and p shall be along the saturation curve, we have

$$\frac{d\lambda}{dT} = c_p - Af'(T)\left\{T\left(\frac{dv}{dT}\right)_p - v\right\}. \tag{9}$$

We may also substitute for $f'(T)$ from (6)

$$\frac{d\lambda}{dT} = c_p + \frac{r}{T} - \frac{r}{u}\left(\frac{dv}{dT}\right)_p + \frac{r}{T}\frac{v'}{u}. \tag{10}$$

This has been called "Planck's equation." The last term is very small and may be neglected. The above form is exact on the basis of our use of heat of liquid and gas at saturation as true "total heat." Other small terms occur when this is not done.

Relation Between Total Heat and Volume.—As remarked, (4) gives a fundamental relation between total heat and volume, and tables or curves from computation or experiment giving these quantities must have the mutual relation shown by (3) or (4). Some well-known steam tables give properties of superheated steam on basis of formulas which confessedly do not satisfy the desired relation. Hence comparison of values of the two sides of (3) computed by interpolation and differences shows some disagreement.

Total Heat and Entropy of an Imperfect Gas from Volume.—By integration of (4) with respect to p, maintaining T constant, we obtain a value for H if we can express the integral of the right hand member. There are two ways in which this might be done.

If there existed a good set of experimental values of volume for a wide range of pressures and temperatures they would give the desired values of H. However such values of volume do not now exist.

The other way is by use of values of volume given by a characteristic equation or equation of state. Many such equations have been proposed for steam and other gases on empirical or semi-rational grounds. We will obtain expressions for total heat and specific heat implied by any such equation.

The general expression for H from integration of (4) is

$$H = -AT^2 \int \left(\frac{d\{v/T\}}{dT}\right)_p dp_T + F(T). \tag{11}$$

This does not completely determine H since it involves $F(T)$ an arbitrary function of T not determined by considerations of volume and which must be evaluated by other means. The integral in (11) is obtained by differentiating v/T with respect to T, considering p a constant and then integrating with respect to p considering T a constant. The order of these operations is immaterial. The evaluation of the integral in this way satisfies every requirement so far as volume relations or characteristic equations are concerned, and the function $F(T)$ must be determined by wholly different considerations. For instance, $F(T)$ could be established by knowledge of values of H for various values of T at a particular value of p.

The fundamental differential equation (3) or (4) uses values of volume v to give variation of total heat H with pressure, from point to point along each isotherm. Hence if we have values of v in general, and an initial value of H at any one point on an isotherm, we can determine all other values of H along that isotherm. We cannot, however, from knowledge of v alone pass from one isotherm to the next, but must have as additional information one initial value of H on each isotherm, corresponding to some pressure or curve of pressures.

The general expression for c_p corresponding to the above value for H is

$$c_p = -AT\int\left(\frac{d^2v}{dT^2}\right)_p dp_T + F'(T). \tag{11A}$$

We will use the notation $\int f(p,\ T)dp_T$ to denote partial integration, that is, integration with respect to p on the assumption that T is a constant. This operation performed on $(df_1/dp)_T$ yields f_1, except for a function of T. That is to say, the partial integral must be completed by addition of a function of T, arbitrary so far as it is concerned.

It is to be noted that this operation $\int \cdots dp_T$ is commutative with any other operations (such as differentiations or integrations) in which p is constant. That is

$$(d\{\int f dp_T\}/dT)_p = \int (df/dT)_p dp_T.$$

We may write such an expression as (11) in the form of a definite integral, that is, one with limits. In such a definite integral the variable which is kept constant must be left with its general value in both upper and lower limits. This is T in the case of (11). The variable with respect to which the integration is performed is replaced respectively by the values given by the upper and lower limits. Usually it will be left with the general value in the upper limit of the integral, and will have some particular value in the lower limit. In the case of (11) the upper limit is obtained later by putting p as p and the lower limit by putting p as 0, in both cases leaving T as T. The term from the lower limit therefore gives the requisite function of T only which must be added after the partial integration with respect to p.

We next determine entropy just as we did total heat. We integrate (8) giving in general

$$\phi = -A\int\left(\frac{dv}{dT}\right)_p dp_T + G(T). \tag{12}$$

Just as in the case of total heat, knowledge of v only gives variation along each isotherm, and in order to pass from one isotherm to another we must have additional information. This is given by similar information for total heat, the relation being given by (1), so that assumption of the value of $F(T)$ fixes $G(T)$. From (11A) and (1)

$$\left(\frac{d\phi}{dT}\right)_p = -A\int\left(\frac{d^2v}{dT^2}\right)_p dp_T + \frac{F'(T)}{T}.$$

Comparison of this with result of differentiation of above value of ϕ shows that

$$G'(T) = \frac{F'(T)}{T},$$

so that

$$\phi = -A\int\left(\frac{dv}{dT}\right)_p dp_T + \int\frac{F'(T)}{T}\,dT. \tag{13}$$

Total Heat and Entropy from Volume and Specific Heat at Zero Pressure.—Callender has proposed to obtain the additional knowledge above referred to by the assumption that the specific heat at pressure "zero" is constant, and Goodenough has empirically adopted a certain variable value instead. We will therefore express total heat as given by (11) in terms of c_{p0} the value of c_p for $p = 0$. In general we suppose c_{p0} a function of T.

We do this by writing (11) as a definite integral, as already mentioned. We may make the lower limit $p = 0$ and this has the effect of adding a function of T only which is permissible. The definite integral now vanishes for $p = 0$ for all values of T. If we further add a function of T whose derivative is the desired value of c_{p0} we satisfy the condition that c_p shall have this value for $p = 0$. The expression thus obtained is a function of p and T. We may add as a constant of integration the result of substitution of p_0 and T_0 for p and T in this function so that it will vanish for p_0 and T_0. We also add the arbitrarily selected initial value of H at p_0 and T_0, which is r_0. This value is then assumed at p_0 and T_0. As a result of thus selecting functions of T only and constants of integration, the general integral (11) of equation (4) gives as the general value of total heat, in terms of specific heat of gas at zero pressure,

$$H = r_0 - A\left[T^2\int_0^p\left(\frac{d\{v/T\}}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} + \int_{T_0}^{T} c_{p_0}\,dT. \tag{14}$$

The integral within the brackets is the result of partially integrating $(d\{v/T\}/dT)_p$ with respect to p, counting T as a constant, and then substituting the limits p and 0 for the variable of integration p. T is to be maintained as the general value T. The resulting expression within the brackets is then to have first p and T and then p_0 and T_0 substituted as limits, for p and T.

It may be remarked that the above expression selects as the arbitrary function of (11),

$$F(T) = AT^2 \int^{p_0} \left(\frac{d\{v/T\}}{dT} \right)_p dp_T + \int_{T_0}^{T} c_{p_0} dT. \tag{15}$$

In addition there are constants of integration involving p_0, T_0, etc.

The bracket in (14) involves four terms, with p and T, 0 and T, p_0 and T_0, 0 and T_0 successively substituted for p and T; in the partial integral of $(d\{v/T\}/dT)_p$ with respect to p with T constant. The first of these is the variable result of the integration and the balance are terms not containing p which we may properly add to the partial integral with respect to p.

We may use the following expression which is equivalent to (14)

$$H = r_0 - A \left[T \int_0^p \left(\frac{dv}{dT} \right)_p dp_T - \int_0^p v dp_T \right]_{p_0 T_0}^{pT} + \int_{T_0}^{T} c_{p_0} dT. \tag{16}$$

The value of c_p in terms of c_{p0} is

$$c_p = - AT \int_0^p \left(\frac{d^2 v}{dT^2} \right)_p dp_T + c_{p_0}. \tag{17}$$

Values of U, c_v and μ on the same basis as that of the above expressions, are given by expressions already mentioned and use of the above values for H and c_p.

The general expression for entropy (13) expressed in terms of c_{p0} gives

$$\phi = \frac{r_0}{T_0} - \left[A \int_0^p \left(\frac{dv}{dT} \right)_p dp_T \right]_{p_0 T_0}^{pT} + \int_{T_0}^{T} \frac{c_{p_0}}{T} dT. \tag{18}$$

This is an expression of the same nature as (14). To sum up the results of this article, we have obtained perfectly general formulas for determination of $H c_p U c_v \mu$ and ϕ when we have given expressions for volume v in terms of p and T and specific heat at zero pressure c_{p0} in terms of T. By insertion of the particular expressions proposed by Callender, Heck or Goodenough we obtain values for the quantities mentioned which necessarily follow. Some of these have been obtained by Callender, Heck and Goodenough by less direct methods.

Saturation Values from Volume and Specific Heat at Zero Pressure.— From the preceding relations we may deduce values for the saturation region. We must, however, have in addition to our knowledge of gaseous volume knowledge of liquid volume, and of specific heat of liquid along some isobar. That is to say, if we have volume as a function of pressure and temperature for both liquid and gas, and specific heat at some one point of each isotherm for both liquid and gas, we can deduce values of total heat, heat of evaporation, etc., for the entire plane, including the saturation region. We therefore suppose that we have values of c_p' and v' so that we can obtain values of H', the total heat of liquid, for any value of p and T, by means of either the exact or approximate formula given in the notation, as well as values of ϕ'. We also suppose we have values of c_{p0} and v so that we can obtain H, the total heat of gas, for any value of p and T by means of (14), as well as ϕ by means of (18).

From this knowledge, we will first deduce the " saturation equation " connecting values of p and T at the edge of condensation and evaporation. The application of the relation

$$dH = Td\phi + Avdp$$

to the change from liquid to gas at the constant values of p and T at saturation, gives

$$H - H' - T(\phi - \phi') = 0. \tag{19}$$

All of the functions in this equation are general expressions in p and T, but the equation is only satisfied if p and T are values at saturation. That is, the equation holds for saturation values of p and T, so that it gives a relation which must exist when p and T have saturation values. *It must therefore be the saturation equation* $f(T) - p = 0$. We will later write the equation explicitly in terms of p and T by substitution of the previously given values of H, H', ϕ and ϕ'.

It is to be noted that this equation can be obtained by direct integration of the Clapeyron equation (6). If H, H', v and v' are general expressions in p and T as already discussed, we write (6) in the form

$$AT(v - v')\frac{dp}{dT} - (H - H') = 0. \tag{20}$$

This is an ordinary differential equation in p and T (not a partial differential equation) which is satisfied only if p and T have saturation values, so that it is the differential equation of the saturation curve. It can be integrated in general and the integral obtained turns out to be (19). To integrate (20) we write it in the form

$$\frac{Av}{T}dp - \frac{H}{T^2}dT - \frac{Av'}{T}dp + \frac{H'}{T^2}dT = 0. \tag{21}$$

It is to be noted that, by virtue of (1) and (2),

$$\left(\frac{d\{H/T - \phi\}}{dT}\right)_p = -\frac{H}{T^2}, \qquad \left(\frac{d\{H/T - \phi\}}{dp}\right)_T = \frac{Av}{T},$$

with similar relations between H', ϕ' and v'. It follows that (21) is an " exact differential equation," and the integral given by these relations is (19).

The Clapeyron equation (6) and the general expression of the saturation equation (19) therefore amount to the same thing, and are not independent relations. In the expression (19) H' and ϕ' are general values for the total heat and entropy of the liquid in terms of p and T. However since (19) holds for saturation values of p and T we can use instead the values of H' and ϕ' on the saturation curve, which we call q and n. Hence we may write (19) in the form

$$H - q - T(\phi - n) = 0. \tag{22}$$

This is an alternate form of the saturation equation, useful if we know q and n directly, as functions of T for instance. H and ϕ are as before general expressions in terms of p and T such as given by (14) and (18).

We will next write the saturation equation as an explicit function of p and T, by substituting in (19) for H and ϕ from (14) and (18). We will substitute for H' and ϕ' the exact expressions in the notation. The saturation equation then becomes

$$\begin{gathered} - r_0\left(\frac{T}{T_0} - 1\right) - A\left[T^2\int_0^p \left(\frac{d\{v/T\}}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} + AT\left[\int_0^p \left(\frac{dv}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} \\ - \int_{T_0}^{T} (c_p' - c_{p0})dT + T\int_{T_0}^{T} \left(\frac{c_p' - c_{p0}}{T}\right) dT - A\int_{p_0}^{p} v' dp_T = 0. \end{gathered} \tag{23}$$

If we may neglect variation of liquid volume, as is the case except near the critical point, the last term becomes $- A(p - p_0)v'$.

An alternate form of this expression of the saturation equation, as well as of all of the preceding equations, may be obtained by substituting the perfectly general form whereby the value of v may be supposed given,

$$v = \frac{RT}{p} - \Delta,$$

where Δ is a small function of p and T, which would vanish for a perfect gas. We may also write

$$\int_{T_0}^{T} c_{p0} dT = c(T - T_0) + \Delta_1,$$

$$\int_{T_0}^{T} \frac{c_{p0}}{T} dT = c \log_n \frac{T}{T_0} + \Delta_2,$$

where Δ_1 and Δ_2 are small functions of T which would vanish if c_{p0} (the gaseous specific heat at zero pressure) were constant, and equal to c.

We may also write, following Callender,

$$\int_{T_0}^{T} c_p' dT = c'(T - T_0) + \Delta_3,$$

$$\int_{T_0}^{T} \frac{c_p'}{T} dT = c' \log_n \frac{T}{T_0} + \Delta_4,$$

where Δ_3 and Δ_4 are very small functions of T, since c_p', the liquid specific heat at constant pressure p_0, is very nearly constant, and equal to c'.

The saturation equation (23) then becomes

$$ART \log_n \frac{p}{p_0} - A\left[\int_0^p \Delta dp_T\right]_{p_0T_0}^{pT} + (T - T_0)\left\{A\left[\int_0^p \left(\frac{d\Delta}{dT}\right)_p dp_T\right]^{p_0T_0} - \frac{r_0}{T_0} - (c' - c)\right\} - A\int_{p_0}^p v'dp_T + T(c' - c)\log_n \frac{T}{T_0} \quad (24)$$
$$+ \Delta_1 - T\Delta_2 - \Delta_3 + T\Delta_4 = 0.$$

A similar reduction could be made in the previous expressions for H, ϕ, H', ϕ', etc.

For the case of a perfect gas and perfect liquid, all of the Δs would vanish and the saturation equation would reduce to the following form,

$$ART \log_n \frac{p}{p_0} - (T - T_0)\left\{\frac{r_0}{T_0} + (c' - c)\right\} + T(c' - c)\log_n \frac{T}{T_0} = 0.$$

This expression has often been deduced directly from $pv = RT$ and the assumption that specific heat of gas and liquid are constant. It is known to give but a very rough approximation.

The above exact forms of the saturation equation, (23) and (24), are hardly suited to direct computation of numerical values of saturation pressure or temperature. Known values from experiment can however be substituted and seen to satisfy the equation, or the trial and error method could be used. Hence we have a theoretical means of obtaining saturation pressure and temperature from knowledge of volume for both liquid and gas, and their limiting values of specific heat. By insertion of the saturation values thus obtained in the general expressions for total heat of liquid and gas, H and H', we obtain total heat of saturated liquid and gas, q and λ. By finding the difference between them, we obtain r the latent heat of evaporation. We could also obtain r from the same initial data by means of the Clapeyron equation (6). However, we have already found that this is merely the differential equation corresponding to our general saturation equation (19) so the two methods of obtaining r amount to the same thing and are bound to give equivalent results. The two methods of course give a useful check on computation work. r is also $T(\phi - \phi')$ at saturation.

The system outlined above starts with the expression (14) for total heat of gas at any point, and by means of the value of H' the heat of the liquid at any point, gives the saturation equation, total heat of saturated gas λ and of saturated liquid q and latent heat of evaporation r.

We could however start with (14) and experimental values of saturation pressure and temperature. We also would require experimental values of liquid volume which need not be accurate, however, except near the critical point.

By substitution of the saturation values in (14) we would obtain values of λ. We could obtain values of r by means of (6). Then from the relation $q = \lambda - r$ values of q would be obtained.

Another variation has been used which starts with values of total heat and volume of saturated liquid, the saturation equation and volume of saturated gas. As a result λ is found by adding q to the value of r computed by means of (6). It must agree with the value of λ found by substituting saturation values in expression for total heat of gas.

In each of the above cases the entropy of saturated gas can be found by the same method as used for λ.

A set of values for v, c_p, λ, r and saturation conditions obtained by use of the preceding relations will of course exactly satisfy the Planck equation (9) or (10) as well as the so-called Clausius equation (7).

Callender, Goodenough and Heck Characteristic Equations for Steam.—Callender[1] has proposed a general expression for gaseous volume

$$v = \frac{RT}{p} - \frac{c^0 T_0^n}{T^n} + v',$$

where R, c^0 and n are constants.

For $p = 0$ Callender takes c_{p0} and c_{v0} both constant and given by the perfect gas relations

$$\frac{c_{p0}}{AR} = \frac{K}{K - 1}, \quad \frac{c_{v0}}{AR} = \frac{1}{K - 1},$$

where K is given by the number of atoms in a molecule and is 5/3, 7/5 and 9/7 respectively for 1, 2 and 3 atoms.

As an additional assumption Callender takes in some cases the value $1/(K - 1)$ (which is also the value of c_{v0}/AR) for the exponent n in the equation for v. For a triatomic gas such as steam this is 3.5. The liquid volume, v', is taken constant. Callender then deduces values for specific heat, etc., for the particular case of his equation, by special methods suited to the form of his relations. All of the results which Callender thus obtains can be obtained directly from the general formulas preceding, and the substitution of Callender's values of v, c_{p0} and n. Callender shows that the saturation pressures computed from his form of (24) agree closely with Peabody's smoothing of Regnault's experiments. He substitutes these values in his form of (14) and obtains values of λ. By subtracting experimental values of q he obtains values of r. These he

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[1] Roy. Soc. Proc., p. 266, 1900.

substitutes in (6) and obtains values of the slope of the saturation curve, $f'(T)$. These should check with values obtained directly from the saturation curve. Callender does not make this check, but the writer has compared with Peabody's first differences and found good agreement.

As stated, Callender bases his work on the assumption that c_p is constant as the pressure approaches zero. Recent experimental work seems to indicate that this is not true owing to dissociation.

Goodenough[1] originally proposed the equation

$$v = \frac{BT}{p} - (1 + ap)\frac{m}{T^n} - c.$$

This was modified somewhat in the later publication.

B, a, m, n and c are constants.

He proposes a variable value for specific heat at zero pressure,

$$c_{p0} = \alpha + \beta T + \frac{\gamma}{T^2}.$$

Goodenough obtains values for the various quantities we have already discussed, by mathematical work suited to his particular case. All of his results can be obtained by the general formulas of the preceding sections. Goodenough did not originally tie up his results with the known saturation values except by showing that the value of c_p computed by inserting the known saturation values in (9) agreed fairly well with the value by direct computation from a formula equivalent to (17). If there had been exact agreement the characteristic equation would have been consistent with the known saturation conditions. Goodenough later at the suggestion of Heck made a similar comparison by means of (6).

Heck[2] has proposed empirical expressions for v and c_{p0} somewhat more complicated than either of the above, but so arranged that there is close agreement with the various experimental values. All of Heck's mathematical work can be carried out by the preceding general formulas.

Van der Waal's equation does not give a simple expression for v as a function of p and T so that it does not readily lend itself to our system of analysis.

Saturation Equation Used Instead of Specific Heat at Zero Pressure.—Up to this point we have supposed that one of the initially given relations in addition to the general value of the volume is the specific heat of gas at zero pressure, and have given the general theory of the particular cases cited by Callender, Goodenough and Heck. We have seen that this leads to an expression for the saturation equation. We now proceed to

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[1] Trans. A. S. M. E., Vol. 34, p. 507, 1912. Univ. of Ill. Bull., No. 75, Sept. 7, 1914.

[2] Trans. A. S. M. E., Vol. 35, p. 391, 1913.

give the mathematical theory of a reversal of this method, in which the saturation equation $f(T) = p$, which is well known from experiment, is used as a basis in addition to the general value of the volume; instead of rather arbitrarily assumed expressions for specific heat at zero pressure. This new method has not yet been used for actual computation work.

As already pointed out (14) was derived by using for the initial value of total heat on each isotherm, that occurring where it crosses the isobar $p = 0$. We now use for the initial value on each isotherm that occurring where it crosses the saturation curve, which is itself derived from the value of total heat of liquid at crossing of the isobar $p = p_0$ and values of liquid volume.

We start with values of liquid volume and specific heat of liquid at $p = p_0$. From the relations given in the notation we determine q the heat of saturated liquid. From the general expression for v and the saturation equation and (6) we determine r. By adding q and r we determine λ, the total heat at saturation values of p and T.

We may then express the general integral (11) in the form

$$H = \lambda - AT^2 \int_{f(T)}^{p} \left(\frac{d\{v/T\}}{dT}\right)_p dp_T.$$

As already remarked T is considered constant and left with its general value in the partial integration with respect to p and then the upper and lower limits respectively substituted for p, leaving T as T in both cases.

In actual use of this method it would probably be best to use tables of q, v at saturation, dp/dT, r and λ, all for successively increasing values of T. Then we could make a table of the function $F(T)$ for various values of T from the relation

$$F(T) = \lambda + AT^2 \int^{f(T)} \left(\frac{d\{v/T\}}{dT}\right)_p dp_T.$$

$F(T)$ is then the function of integration in (11) so that we can use (11) to give total heat.

Entropy of gas in general can be found by a similar process. By means of the formula in the notation we can compute n the entropy of saturated liquid, and from r computed as above we can obtain $n + r/T$ the entropy of saturated gas. Then we can express the general integral (12) in the form

$$\phi = n + \frac{r}{T} - A \int_{f(T)}^{p} \left(\frac{dv}{dT}\right)_p dp_T.$$

As in the preceding case we could make a table of the function $G(T)$ from the relation

$$G(T) = n + \frac{r}{T} + A \int^{f(T)} \left(\frac{dv}{dT}\right)_p dp_T.$$

$G(T)$ is the function of integration in (12) so that we can use (12) to give entropy.

Another form in which we could handle this computation of $F(T)$ and $G(T)$ for use in (11) and (12) is as follows.

A table would be made of the auxiliary function y for various values of T from the relation

$$y = A \int^{f(T)} (v - v')dp_T + A \int^{p_0} v'dp_T.$$

By means of a curve, or differences from the table for y, we would next find values of dy/dT and $d(y/T)/dT$. These values could also be found from the following relations, but this would probably be more difficult.

$$T^2\frac{d(y/T)}{dT} = AT^2 \int^{f(T)} \left\{ \frac{d(\{v - v'\}/T)}{dT} \right\}_p dp_T + ATuf'(T)$$
$$+ AT^2 \int^{p_0} \left(\frac{d\{v'/T\}}{dT} \right)_p dp_T,$$

$$\frac{dy}{dT} = A \int^{f(T)} \left\{ \frac{d(v - v')}{dT} \right\}_p dp_T + Auf'(T) + A \int^{p_0} \left(\frac{dv'}{dT}\right)_p dp_T.$$

If we may take the liquid volume v' as constant for all values of T all of this work is much simplified.

It then follows that the functions in (11) and (12) are given by the relations

$$F(T) = \int_{T_0}^{T} c_p'dT + T^2\frac{d(y/T)}{dT},$$

$$G(T) = \int_{T_0}^{T} \frac{c_p'}{T} dT + \frac{dy}{dT}.$$

We have also

$$c_p = - AT \int \left(\frac{d^2v}{dT^2}\right)_p dp_T + c_p' + T\frac{d^2y}{dT^2}.$$

From the latter expression we can find the value, previously assumed arbitrarily, of the specific heat at zero pressure, c_{p0}, which follows from the use of the saturation equation. This is done by substituting $p = 0$ in the first integral of the last equation, if our expression for v is valid for such value of p. However our values are legitimate in the finite region even if the values of v and c_{p0} are indeterminate for $p = 0$. For this reason the system of the present section whereby initial values are established by the known saturation condition, is preferable to establishment by the conditions in the mythical region where p is zero.

It is probable that all substances at all temperatures are theoretically gaseous at zero pressure so that every gaseous isotherm crosses the isobar $p = 0$, and so that the assumption of c_p for $p = 0$ theoretically determines the desired initial values. However the volume is infinite, and the number of molecules negligible, and the degree of association of the molecules unknown, and conditions in general so far removed from those with which we usually work, that exterpolation from one region to the other involves considerable assumption.

Volume from Values of Total Heat.—Up to this point we have supposed v given by some sort of characteristic equation and have computed total heat and entropy from it. If, however, we have experimental or other data regarding total heat, we can by a reverse process obtain values of volume.

We do this by partial integration of (4) which gives values of v/T except for an indeterminate function of T referred to later. We must have as a starting point values of $(dH/dp)_T$ for various values of p and T. A general expression for total heat in terms of pressure and temperature, if it existed, would of course give this by direct differentiation. Dr. Davis has also proposed the use of experimental values of μ and c_p and the identity already alluded to,

$$-\mu c_p = \left(\frac{dH}{dp}\right)_T,$$

in conjunction with saturation volumes as discussed below.

As remarked, the partial integration of (4) must be completed by addition of some function of p, arbitrary as far as (4) is concerned, and to be determined by other considerations. (4) gives merely variation of v as T changes for any value of p but gives no information regarding the variation of v with p. We must have, from some other source, a chain of values of v for different values of p, so as to establish one value of v on each isobar. (4) then gives all other values of v on an isobar. Such a series of values would be furnished by the volume of the saturated gas. These could in turn be furnished by the total heat of the gas and the volume of the liquid at saturation. That is, the necessary chain of values of volume could be volumes of liquid if we have total heat and saturation data.

We have as the general integral of (4)

$$v = -JT\int \frac{1}{T^2}\left(\frac{dH}{dp}\right)_T dT_p + T\psi(p).$$

If we have means of determining the saturation volume v_p in terms of pressure we can use the following form of the integral

$$v = -JT\int_{f^{-1}(p)}^{T}\frac{1}{T^2}\left(\frac{dH}{dp}\right)_T dT_p + Tv_p. \qquad (25)$$

This gives volume of superheated gas for any temperature and pressure, where the saturation volume v_p and the lower limit of the integral are values for the pressure in question at saturation temperature.

Obviously we can also obtain total heat from the knowledge already supposed, of values of $-\mu c_p$ which is $(dH/dp)_T$ and c_p which is $(dH/dT)_p$, the value being

$$H = r_0 + \int_{p_0T_0}^{pT} - \mu c_p dp_T + \left[\int c_p dT_p\right]_{p_0}^{p} \text{(terms in } p \text{ only)},$$

or

$$H = r_0 + \int_{p_0T_0}^{pT} c_p dT_p + \left[\int - \mu c_p dp_T\right]_{T_0}^{T} \text{(terms in } T \text{ only)}.$$

From such a value of total heat in general the value at saturation, λ, would be found by substituting saturation values, and the latent heat r would be found by subtracting q, the heat of the liquid given by equations in the notation. These values of λ and r would probably be shown more conveniently by tables than by equations.

The value of saturation volume v_p alluded to above, may be obtained by (6), or must check with (6), using r as above.

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PHYSICAL REVIEW.

THE THOMSON EFFECTS IN TUNGSTEN, TANTALUM AND CARBON AT INCANDESCENT TEMPERATURES DETERMINED BY AN OPTICAL PYROMETER METHOD.

By A. G. Worthing.

Introduction.

THE present paper is a direct outcome of certain effects noted in connection with a study by Hyde, Cady and Worthing[1] of the energy losses in electric incandescent lamps. Favorable conditions for observing the Thomson effect exist in such lamps in consequence of the high temperature gradients in the neighborhood of the leading-in junctions and of the large current densities. W. König,[2] using a visual method, has obtained qualitative results on Pt, Cu, Fe and constanstan. However, so far as the writer knows, no quantitative results have been obtained hitherto in connection with incandescent temperatures. An optical pyrometer method for such measurements and its application are here described.

Theory.

Consider a small filament of uniform surface and cross-section mounted in an evacuated bulb and heated to incandescence by an electric current. For the temperature distributions in the neighborhood of a cooling junction for a given intensity of heating current, three cases are to be distinguished depending on whether the heating current through the filament (1) is a direct current directed away from the junction, (2) is a direct current directed toward the junction, or (3) is an alternating current. In Fig. 1 (a diagrammatic representation for tungsten) the curves A_1, A_2 and A_3 respectively represent the distributions of the rates of production of heat per unit of radiating surface, w_1, w_2 and w_3 (Table I.); and the curves B_1, B_2 and B_3 respectively the radiation intensities E_1, E_2 and

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[1] Illum. Eng. (Lond.), *4*, p. 389, 1911. Trans. Illum. Eng. Soc. (U. S.), *6*, p. 238, 1911.

[2] Phys. Zeit., *11*, 1913, 1910.

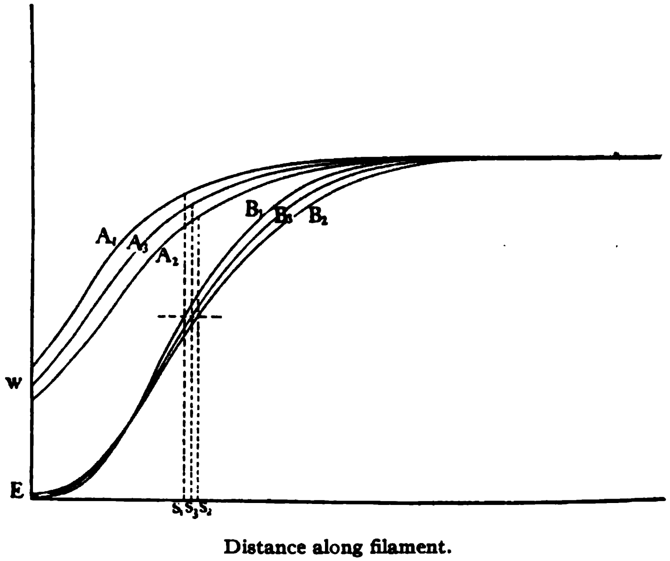

Fig. 1.

Diagrammatic representation for a portion of a tungsten filament near a cooling junction, of the distributions of the rates of development of heat in the elements of filament per unit of radiating surface (A_1, A_2, A_3) and of the radiation intensities (B_1, B_2, B_3) respectively for the conditions that the heating current is (1) directed away from the cooling junction, (2) directed toward the cooling junction, and (3) alternating.

TABLE I.

Symbols and Quantities Used.

w = Rate of development of heat in an element of filament per unit of radiating surface.
E = Radiation intensity.
l = Distance along filament.
r = Radius of filament.
I = Current.
ρ = Resistivity.
T = Temperature.
σ = Coefficient of the Thomson effect.
$\frac{dH}{dT}$ = Rate of heat conduction along the filament at a given cross-section.
k = Thermal conductivity.
p = Constant defined by equation (8).
μ = Constant of equation (12).
E_m and T_m = Maximum values of E and T.

E_3. Methods for obtaining curves B_1, B_2, B_3 and A_3 are fully described by the author[1] elsewhere. A method which may be employed in obtaining curves A_1 and A_2 will appear from later considerations. The crossing of the B curves has no particular significance from the standpoint

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[1] PHYS. REV., II., 4, p. 535, 1914.

of the Thomson effect. It is merely a consequence of the lateral displacements of these curves due to the Peltier effect at the junction.

For the rates w_1 and w_2 corresponding to the condition $E_1 = E_2$ and thus necessarily $T_1 = T_2$ (positions S_1 and S_2, Fig. 1), we have, from the standpoint that the heating per unit length of filament must equal the sum of the Joulean and the Thomson heatings,

$$2\pi r w_1 = \frac{I^2\rho}{\pi r^2} - \sigma I \frac{dT}{dl_1}, \tag{1}$$

and

$$2\pi r w_2 = \frac{I^2\rho}{\pi r^2} + \sigma I \frac{dT}{dl_2}, \tag{2}$$

in which the sign of the coefficient σ is taken as positive when the gradient of the Thomson E.M.F. coincides in direction with the temperature gradient. For tungsten as is shown in Fig. 1, σ is negative. (1) and (2) give directly

$$\left[\sigma = \frac{2\pi r(w_1 - w_2)}{I\left(\frac{dT}{dl_1} + \frac{dT}{dl_2}\right)}\right]_{T_1=T_2=T}. \tag{3}$$

In order to make use of (3), a method of obtaining the distributions of w_1 and w_2 must be devised. Since the rate of heat production in an element of filament must equal the sum of the rate of radiation of energy from it and of the *net* rate of heat conduction from it, there results

$$2\pi r w = 2\pi r E - \frac{d}{dl}\left(\frac{dH}{dt}\right), \tag{4}$$

where dH/dt represents the rate of conduction of heat across the cross-section of filament at l. Since

$$\frac{dH}{dt} = \pi r^2 k \frac{dT}{dl}, \tag{5}$$

there follows

$$\frac{d}{dl}\left(\frac{dH}{dt}\right) = \pi r^2\left[k\frac{d^2T}{dl^2} + \frac{dk}{dT}\left(\frac{dT}{dl}\right)^2\right]. \tag{6}$$

Equations (4) and (6) give

$$w = E - \frac{r}{2}\left[k\frac{d^2T}{dl^2} + \frac{dk}{dT}\left(\frac{dT}{dl}\right)^2\right]. \tag{7}$$

Determinations of k as a function of T and of T and E as functions of l, such as the writer has reported in the papers already referred to, enable one to obtain the desired distributions of w_1 and w_2 as functions first of E_1 and E_2 and then of l. The relations thus obtained suffice for obtaining σ.

A simplification results if a certain condition as to the distributions of E_1 and E_2 exists. This condition, which was found experimentally to hold, is

$$\left[\frac{dT}{dl_2} = p\frac{dT}{dl_1}\right]_{T_1=T_2=T}, \tag{8}$$

in which p is a constant depending on the material of the filament and on the maximum filament temperature. Then since the distribution of E_3 is approximately if not accurately a mean of the distributions of E_1 and E_2, this condition may be rewritten as

$$\left[\sqrt{p}\frac{dT}{dl_1} = \frac{1}{\sqrt{p}}\frac{dT}{dl_2} = \frac{dT}{dl_3}\right]_{T_1=T_2=T_3=T}. \tag{9}$$

Since as indicated in (8) and (9) the points considered on the different temperature distribution curves refer to cross-sections having the same temperature, l_1 and l_2 may be expressed as functions of l_3. This leads to

$$\left[p\frac{d^2T}{dl_1^2} = \frac{1}{p}\frac{d^2T}{dl_2^2} = \frac{d^2T}{dl_3^2}\right]_{T_1=T_2=T_3=T}. \tag{10}$$

Equations (3) and (7) when combined subject to (9) and (10) give finally

$$\sigma = \frac{\pi r^2}{2I}\left(p - \frac{1}{p}\right)\frac{k\dfrac{d^2T}{dl_3^2} + \dfrac{dk}{dT}\left(\dfrac{dT}{dl_3}\right)^2}{\dfrac{dT}{dl_3}}. \tag{11}$$

RESULTS.

As indicated in the paper already referred to, the temperature distribution along an incandescent tungsten filament in vacuo is of the type

$$\frac{T}{T_m} = [1 - e^{-\mu(l+l_0)}]^{1.87}. \tag{12}$$

Such a temperature distribution curve and the corresponding radiation intensity distribution curve were platted for a particular tungsten filament (r = 0.01045 cm.) heated by a current of 4.32 amps. to a maximum temperature of 2315° K. (scale of Mendenhall and Forsythe).[1] In Fig. 2 there are platted the two individual distributions of radiation intensity depending on the direction of flow of the D.C. heating currents, from which the previously mentioned curves were obtained. As platted they are approximately straight lines. As has been stated before in connection with the other related curves, the deviations, with the exception of those near the cooling junction, are accidental. The conclusion as to the constancy of p resulted from a large number of such tests. In Table II.

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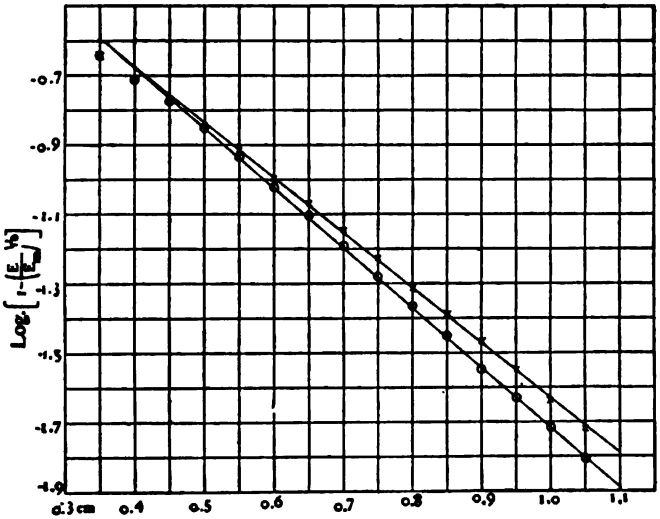
[1] Astrophys. Jour., 37, p. 380, 1913.



Distance along filament.

Fig. 2.

The radiation intensity distribution for a particular tungsten filament ($r = 0.01045$ cm.) heated to a maximum temperature of 2315° K., by (1) a current of 4.32 amps. directed away from the cooling junction (⊙ ⊙ ⊙), and (2) by a current of the same intensity directed toward the cooling junction (× × ×).

Table II.

Data Necessary for the Application of (11) to a Particular Tungsten Filament, and Computed Values of the Thomson E.M.F. Coefficient.

Condition.	Maximum Filament Temperature.	Average Value of p.	r	I	μ
1	2315° K.	0.920	0.01045 cm.	4.32 amp.	$3.80 \frac{1}{\text{cm.}}$
2	1890	0.955	0.01045	2.88	2.65

Condition 1.		Condition 2.	
Temperature in ° K.	σ in $\frac{\text{Microvolts}}{\text{Degree}}$.	Temperature in ° K.	σ in $\frac{\text{Microvolts}}{\text{Degree}}$.
2200	−35	1800	−16
2000	−28	1600	−11
1800	−21	1500	−10

there are given the average values of p for two maximum filament temperatures. The value for 1890° K. is considerably more uncertain than that for 2315° K. There are given also other data necessary in the application of these two values by means of (11), together with the results. The lower temperature in each case refers to a region in which the fit of (12) indicates the application of (11) as being still justifiable. The lack of agreement of the two values for 1800° K., on the assumption that σ is independent of the current density, is probably ascribable to the comparatively great difficulty experienced in condition 2 in determining the value of p. That thermionic currents can not account for the difference seems evident when one considers the maximum potential difference of approximately 20 volts between the terminals of the lamp filament in conjunction with the work of Langmuir.[1]

The results obtained for filaments of tantalum and of untreated carbon are indicated in Table III. The temperature calibrations here used are also those of Mendenhall and Forsythe.[2]

TABLE III.

Thomson Effect in Tantalum and Carbon.

Tantalum.		Carbon.	
Temperature in ° K.	σ in $\frac{\text{Microvolts}}{\text{Degrees}}$.	Temperature in ° K.	σ in $\frac{\text{Microvolts}}{\text{Degree}}$.
2100	+24	2100	−22
1900	+20	2000	−21
1700	+16	1800	−19

The greatest uncertainty in this work lies in the fact that the relations $E = \varphi(T)$ and $E = f(l)$ [relations (5) and (6) of previous paper on thermal conduction] are determined at different portions of the filament under experiment. This means a difference in the two cases in the glassware between the background filament and the pyrometer filament and also possible inequalities in the cross-sections of the filament. Due to the many filaments of tungsten which have been investigated, the uncertainty there has been largely reduced but such is not the case with carbon or tantalum. It is possible to eliminate largely this source of error by using metal cases with plate glass windows, with a device for clamping and unclamping the filament in the neighborhood to be studied.

SUMMARY.

1. A method of studying quantitatively the Thomson effects in filaments mounted in evacuated chambers, with the aid of an optical pyrometer, has been developed.

2. The Thomson E.M.F. coefficients have been determined for tungsten, tantalum and carbon (Tables II. and III.) for temperatures ranging from 1500° K. to 2200° K.

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[1] PHYS. REV., II., 2, p. 450, 1913.

[2] Astrophys. Jour., 37, p. 380, 1913.

The writer is indebted to Messrs. K. Linder, G. Cadisch, A. Shapero and A. Scheel for efficient aid in the experimental work, and particularly to Dr. E. P. Hyde, for first suggesting the quantitative determinations here recorded.

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January, 1915.

MUTUAL INDUCTANCES OF CIRCUITS COMPOSED OF STRAIGHT WIRES.

By George A. Campbell.

THE mutual inductance between any two circuits made up of m and n straight wires of negligible diameter may be most simply expressed as the sum of the mn mutual Neumann integrals between the sides taken in pairs, one from each circuit. As such inductances are required in practical computations, it is desirable to have a formula for the mutual Neumann integral between two skew lines of any lengths in any relative location. The Bureau of Standard's collection of "Formulas and Tables for the Calculation of Mutual and Self-Induction (Revised)" does not contain such a formula and the only statement of the result[1] which I have seen is involved and unsatisfactory for actual use. A general formula in convenient form, formulas for a number of special cases, a diagram for use in calculations, and, finally, the deduction of the formulas follow.

To speak of the self and mutual inductances of circuits one or both of which are unclosed, is logically inexact and practically unsafe, for it tends to vague thinking and the entire neglect of the return circuit in cases where the effect of the return is easily lost sight of because it is at a remote distance. Heaviside advocated the exclusive consideration of closed circuits, securing external continuity in every case by means of two superposed uniform radial systems, one diverging from the positive terminal in all directions, the other converging on the negative terminal from all directions. This means subtracting one half of the second order difference $(-Aa+Ab+Ba-Bb)$ of the distances between the terminals $A, B; a, b$, from the Neumann integral for any unclosed circuits between these terminals. A better way, it seems to me, is to continue using the Neumann integrals for unclosed circuits but to refer to them as the self or mutual Neumann integrals according as the two unclosed circuits are or are not identical. This reserves the terms self and mutual inductances for use with closed circuits exclusively. The following results are expressed in this way.

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[1] Martens, F. F., Ann. der Phys., 29, p. 959, 1909.

NEUMANN INTEGRAL FOR SKEW LINES.

The mutual Neumann integral between any two straight filaments AB, ab, the positive directions A to B and a to b making with each other the angle e $(0 \ngtr e \ngtr \pi)$, is

$$\left.\begin{aligned}
N &= \underline{pB'}\log\frac{Bb+\underline{B'b}}{Ba+\underline{B'a}} - \underline{pA'}\log\frac{Ab+\underline{A'b}}{Aa+\underline{A'a}} + \underline{Pb'}\log\frac{bB+\underline{b'B}}{bA+\underline{b'A}} \\
&\qquad - \underline{Pa'}\log\frac{aB+\underline{a'B}}{aA+\underline{a'A}} - \frac{Pp\Omega}{\tan e} \\
&= 2\underline{pB'}\tanh^{-1}\frac{ab}{aB+Bb} - 2\underline{pA'}\tanh^{-1}\frac{ab}{aA+Ab} \\
&\qquad + 2\underline{Pb'}\tanh^{-1}\frac{AB}{Ab+bB} - 2\underline{Pa'}\tanh^{-1}\frac{AB}{Aa+aB} - \frac{Pp\Omega}{\tan e}
\end{aligned}\right\} \tag{1}$$

where $A'B'$, $a'b'$ are the projections of AB and ab on each other; Pp is the common perpendicular to AB, ab taken positive, as are all other distances except those (underscored) measured along AB and ab which are taken algebraically positive in the directions AB and ab respectively; Ω is the (positive) solid angle subtended at B by a parallelogram $abcd$ constructed on ab with bc parallel and equal to AB.[1]

SPECIAL CASES.

1. Filaments mutually perpendicular, $N = 0$.

2. Filaments starting from a common point $(P = A = p = a)$,

$$N = \underline{A'B'}\log\frac{Bb+\underline{B'b}}{AB+\underline{B'a}} + \underline{a'b'}\log\frac{bB+\underline{b'B}}{ab+\underline{b'A}}. \tag{2}$$

3. Filaments mutually parallel $(e = 0 \text{ or } \pi)$,

$$\begin{aligned}
N = AB\log\frac{aB+\underline{a'B}}{bB+\underline{b'B}} + \underline{Ab'}\log\frac{bB+\underline{b'B}}{bA+\underline{b'A}} - \underline{Aa'}\log\frac{aB+\underline{a'B}}{aA+\underline{a'A}} \\
-(-Aa+Ab+Ba-Bb)
\end{aligned} \tag{3}$$

3*a*. If $e = 0$, and the midpoints of AB and ab are opposite each other.

$$N = AB\log\frac{2Ab+AB+ab}{2Aa+AB-ab} + ab\log\frac{2Ab+AB+ab}{2Aa+ab-AB} + 2Aa - 2Ab, \tag{3a}$$

4. Filaments mutually parallel beginning at a common perpendicular, with positive direction either the same or opposite $(e = 0 \text{ or } \pi,\ Aa = Pp)$,

$$N = AB\log\frac{aB+AB}{bB+\underline{b'B}} + ab\log\frac{Ab+ab}{Bb+\underline{B'b}} - (-Aa+Ab+Ba-Bb) \tag{4}$$

---

[1] Formula 10 may be used for Ω.

$$\left.\begin{aligned} &= 2AB \log \frac{aB + AB}{Aa} - 2(Ab - Aa) \\ &= 4AB \tanh^{-1} \frac{AB}{aB + Bb} - 2Ab + 2Aa \\ &= 2AB \left(\log \frac{2}{t} - 1 + t - \frac{t^2}{4} + \frac{t^4}{32} - \frac{t^6}{96} \right. \\ &\qquad \left. + \frac{5t^8}{32.32} - \cdots \right), \quad t = \frac{Aa}{AB} \end{aligned} \right\} \text{if } AB = ab,\ e = 0 \quad (5)$$

$$\left.\begin{aligned} &= 2AB \log \frac{aB + AB}{bB + 2AB} - (-Aa + 2Ab - Bb) \\ &= 2AB \left(- \log 2 + \frac{t}{2} - \frac{3t^2}{16} + \frac{15t^4}{16.32} - \frac{63t^6}{64.96} \right. \\ &\qquad \left. + \frac{5.255t^8}{16.16.32.32} - \cdots \right), \quad t = \frac{Aa}{AB} \end{aligned} \right\} \text{if } AB = ab,\ e = \pi. \quad (6)$$

5. Non-overlapping portions of a straight filament $ABab$ ($e = 0$, $Pp = 0$)

$$\begin{aligned} N &= AB \log \frac{Ab}{Aa} + ab \log \frac{Ab}{Bb} + Ba \log \frac{Ab \cdot Ba}{Aa \cdot Bb} \\ &= - Aa \log Aa + Ab \log Ab + Ba \log Ba - Bb \log Bb. \end{aligned} \quad (7)$$

6. Filament ab with the element at the point s having the algebraic projection dx on filament AB.

$$\begin{aligned} dN &= \log \frac{sB + \underline{s'B}}{sA + \underline{s'A}} dx \\ &= 2dx \tanh^{-1} \frac{AB}{As + sB}, \end{aligned} \quad (8)$$

RULE FOR USING THE DIAGRAM OF CONFOCAL ELLIPSES (FIG. 1) FOR FINDING THE MUTUAL NEUMANN INTEGRAL BETWEEN A FINITE STRAIGHT LINE AB AND ANY OTHER LINE ab.

Draw the two lines on such a scale that A, B coincide with the foci; if AB and ab do not both lie in one plane bring ab into the plane of the paper by rotating it point by point about the right line through AB. Consider the ellipses to be contour lines with the elevations noted upon them. Determine the projection upon the vertical plane through the foci A, B of the vertical cylindrical surface erected upon ab and bounded by the contour surface, considering areas to be positive or negative according as the projection of ab has or has not *the same positive direction as AB. If horizontal distances have been measured in 10^9 cm. the area found is the mutual integral in henries.*

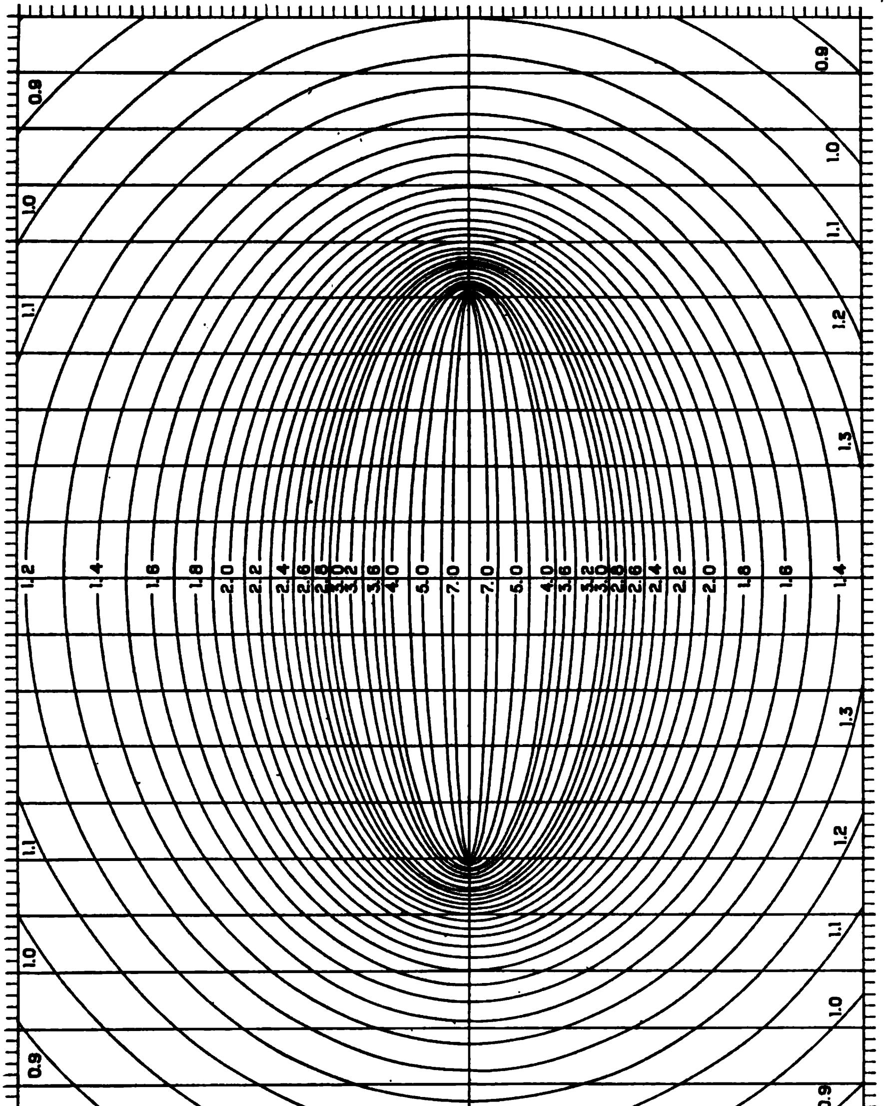

Fig. 1.
Confocal Ellipse Diagram for Calculating Mutual Neumann Integrals.

Transformations of Formula I.

Formula (I) may be thrown into a variety of equivalent forms by means of the following geometrical relationships for the first ratio occurring in the logarithmic terms, which is typical of all, and for the solid angle, the expression for which is in terms of the dihedral angles of the tetrahedron on AB, ab.

$$\begin{aligned}\frac{Bb+\underline{B'b}}{Ba+\underline{B'a}}&=\frac{Ba-\underline{B'a}}{Bb-\underline{B'b}}=\frac{(Bb+\underline{B'b})(Ba-\underline{B'a})}{B'B^2}\\&=\cot\frac{\angle Bab}{2}\cot\frac{\angle Bba}{2}=\frac{Ba+Bb+ab}{Ba+Bb-ab}=e^{2\tanh^{-1}\frac{ab}{aB+Bb}},\end{aligned}\tag{9}$$

$$\begin{aligned}\Omega=\tan^{-1}\left(\frac{Pp}{Bb}\cot e+\frac{PB}{Pp}\frac{pb}{Bb}\sin e\right)-\tan^{-1}\left(\frac{Pp}{Ba}\cot e+\frac{PB}{Pp}\frac{pa}{Ba}\sin e\right)\\-\tan^{-1}\left(\frac{Pp}{Ab}\cot e+\frac{PA}{Pp}\frac{pb}{Ab}\sin e\right)+\tan^{-1}\left(\frac{Pp}{Aa}\cot e+\frac{PA}{Pp}\frac{pa}{Aa}\sin e\right).\end{aligned}\tag{10}$$

PROOFS.

The Neumann integral is

$$N=\cos e\int\int\frac{dSds}{r},\qquad\text{where } r^2=Pp^2+S^2-2Ss\cos e+s^2$$

if S, s are measured in the positive directions along AB, ab respectively from the common perpendicular Pp. As is easily shown by performing the indicated differentiations, the integral for N may be written in the following directly integrable form.

$$\begin{aligned}N&=\cos e\int\int\left(D_S\frac{S}{r}+D_s\frac{s}{r}-\frac{Pp^2}{r^3}\right)dSds\\&=\cos e\left(\left|S\int\frac{ds}{r}\right|+\left|s\int\frac{dS}{r}\right|-\frac{Pp}{\sin e}\int\int\frac{Pp}{r^3}\sin e\,dSds\right)\\&=\cos e\,\Bigg\|\,S\log(r+s-S\cos e)+s\log(r+S-s\cos e)\\&\qquad-\frac{Pp\text{ (solid angle)}}{\sin e}\left|\begin{array}{c}S=\underline{PB}\\ \\ S=\underline{PA}\end{array}\right|\begin{array}{c}s=\underline{pb}\\ \\ s=\underline{pa}\end{array}.\end{aligned}$$

the solid angle being given by the last integral, as ($\sin e\;dSds$) may be taken as an element of area of the parallelogram $abcd$ in oblique coördinates (if $\sin e$ is positive which requires that e shall lie between 0 and π), the factor Pp/r reduces this to its projection normal to r, and division by r^2 gives the solid angle subtended by the element. Introducing the limits and substituting $\underline{PB}\cos e=\underline{pB'}$, etc., give formula (1).

This Neumann integral is also (1) the Newtonian potential at B of the parallelogram $abcd$ with a uniform mass equal to $\cot e$ per unit area, which suggests other ways of performing the integration; (2) the mutual potential of two rods AB, ab with the mass $\sqrt{\cos e}$ per unit length; (3) the mutual Neumann integral for any arc of a hyperbola and any part of the conjugate axis as is shown below.

Formula (3) is obtained by taking Pp coincident with AA' and changing the first term so as to substitute algebraical quantities measured along AB in place of the algebraical quantities measured along ab. This change is made by noting that for any pair of points X, y on parallel filaments and their projections X', y' the following relations hold, $\underline{X'y} = \pm \underline{Xy'} = \mp \underline{y'X}$, the upper and lower signs applying to positive directions in the same or opposite sense respectively; whence

$$\underline{A'B'} \log \frac{Bb + \underline{B'b}}{Ba + \underline{B'a}} = \pm AB \log \frac{Bb \mp \underline{b'B}}{Ba \mp \underline{a'B}} = AB \log \frac{aB + \underline{a'B}}{bB + \underline{b'B}}.$$

The solid angle term becomes o/o but may readily be evaluated, or it may be derived directly from the indefinite integral for this term, which is found to reduce to $\| r \|$ for parallel filaments as $D_S D_s r = - Pp^2 r^{-3} \cos e$ for this case, and substituting this makes the term directly integrable. As the location of Pp is arbitrary, any one of the four terms in (1) may be made to vanish by locating Pp at A, B, a or b. The logarithmic terms may, if desired, be so combined as to be symmetrical in the quantities involved.

Formula (4) is a special case of (3). Formula (5) is the well-known result for the opposite sides of a rectangle, and formulas (3), (4) and (6) may all be derived from it, in spite of the fact that it is merely a special case of (3) and (4).

Formula (7) holds only for the particular sequence of points indicated, but any non-overlapping sequence may be readily reduced to this. The second expression is the one which is most readily obtained by direct integration of Neumann's integral, for that gives $\| - r \log r \|$ for the indefinite integral in this special case.

Formula (10) (which corresponds to the indefinite integral $\| \tan^{-1} ((Pp^2 \cot e + Ss \sin e)/Ppr)) \|$ for the solid angle expressed in terms of the dihedral angles may be checked by differentiating with respect to both S and s, or it may be derived by geometrical considerations.

Formula (8) expresses the mutual Neumann integral between any filament ab and any straight filament AB in terms of the projections of the elements of ab on AB multiplied by factors which depend only upon the location of the elements with respect to AB. A diagram showing the value of this factor at every point may be used for determining the value of the integral for any particular filament ab. To find the locus of the point s for constant values of this factor, it is sufficient to notice that formula (8) (second form) remains unchanged if the denominator $(As + sB)$ is constant, which gives an ellipse with foci at A and B; the ellipticity $= AB/(As + sB)$ is, by formula (8), equal to tanh $(dN/2dx)$. A family of confocal ellipses has therefore been drawn for different values of dN/dx, and is reproduced in the accompanying figure. Since rotating the elements of ab about AB does not change formula (8), the diagram may be used for all lines including those which do not lie in the plane of AB by following the directions given above. The accuracy obtainable in this method of calculating Neumann integrals depends only upon the number of ellipses shown on the diagram and the precision of the graphical work.

The rotation of a finite straight skew filament ab point by point about AB into the plane of AB, Pp changes it into an arc of a hyperbola having the common perpendicular Pp for a semi-transverse axis and asymptotes through P making the angle e with AB. For, take any point s on ab and set $ss' = x$, $Ps' = y$, then

$$x^2 = y^2 \tan^2 e + Pp^2$$

or

$$\frac{x^2}{Pp^2} - \frac{y^2}{Pp^2 \cot^2 e} = 1.$$

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THE VARIATION WITH METEOROLOGICAL CONDITIONS OF THE AMOUNT OF RADIUM EMANATION IN THE ATMOSPHERE, IN THE SOIL GAS, AND IN THE AIR EXHALED FROM THE SURFACE OF THE GROUND, AT MANILA.

By J. R. Wright and O. F. Smith.

IN the Philippine Journal of Science of February, 1914, the authors published the results of an extensive series of observations on the amount of radium emanation in the atmosphere of Manila. The well-known charcoal-absorption method was used and the main part of the investigation was preceded by numerous tests on certain points concerned with the accuracy of the method. The work at Manila was supplemented by an investigation of the variation of the emanation content of the atmosphere with altitude, observations being taken on Mt. Pauai, elevation 2,460 meters, and the results compared with those for sea level.[1]

Although the especial points of the investigation were those above mentioned we felt justified at that time, since the period involved extended over almost a year and a half, in pointing out certain evident relations between the emanation content of the atmosphere and the different meteorological factors. The data at our command was not considered sufficient, however, to justify the drawing of more than very general conclusions. During the past year observations have been taken with the object of determining more definitely to what extent the amount of radium emanation in the air is dependent on weather conditions. At the same time tests have been made on several other points which have a more or less direct bearing on the question.

The experimental method used was described in detail in our previous paper, but for the sake of completeness a brief summary of the description will be given, together with such modifications as experience had shown to be advisable.

The method had its origin in the discovery by Rutherford that charcoal made from the shells of coconuts possesses the property of absorbing radioactive emanations. Eve[2] and Satterly[3] independently applied the discovery to the determination of the radium-emanation content of the atmosphere.

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[1] Phys. Zeit., *15*, 31, 1914.

[2] Phil. Mag., *14*, 724, 1907.

[3] Phil. Mag., *16*, 584, 1908.

To attain this end air was passed at a known rate and for a definite length of time through a tube containing coconut charcoal, which absorbed the emanation from the air. At the same time air was bubbled through a solution of radium bromide, containing a known amount of radium, and the emanation from the solution and the air collected in another charcoal tube. The emanation absorbed in the charcoal was then driven off by heating, collected over water in aspirators, and finally measured by passing into an ionization chamber connected either with an electroscope or an electrometer. By this method quantitative determinations of the amount of radium emanation in the atmosphere can be obtained, and since the method is a comparative one the results should be independent of variations in the pressure, humidity, and nucleation of the air, which is a serious objection to the extensively used active-deposit method.

Since in the present investigation the object was to determine the variation of the emanation content of the air with weather conditions it was essential that all observations should be taken under identical experimental conditions and in the same manner. Having had two years experience in taking similar observations we were able to attain this end with certainty. Throughout the thirteen months covered by this series of experiments the arrangement of apparatus and the method of procedure in taking observations was never varied. Consequently, the results should at least show quantitatively the variation of the amount of emanation in the atmosphere.

EXPERIMENTAL PROCEDURE.

Collecting.—The air to be tested was drawn in through a tube, projecting from a second story window of the Bureau of Science, by means of a motor driven oil pump. By placing several large bottles, having a total capacity of about 50 liters, in series with the pump a constant rate of flow could be maintained for any desired length of time. The rate of flow was determined by means of accurately calibrated oil manometers across glass capillary tubes of fairly small bore. The air stream was regulated by means of easily adjusted pinch cocks on rubber tubing.

To extract the dust from the air a tube containing cotton wool was placed between the intake and a large distributing bottle. From the distributing bottle the air was divided into two exactly equal parts, one part passing through the branch containing the radium bromide solution and the other part through an exactly similar system, with the exception of that part connected with the standard solution. In both branches the air was thoroughly dried by bubbling it first through sulphuric acid and then passing it over calcium chloride.

The coconut charcoal was contained in electro-silica tubes having a uniform bore of 1.5 cm. In each tube there was placed 70 grams of finely granulated coconut charcoal, which was firmly packed and held in place by long plugs of asbestos wool. Experience had shown the importance of keeping the charcoal firmly and uniformly packed if the same fraction of the total amount of emanation passing through the tubes was to be absorbed in every case. Two of these tubes were placed in series in each branch of the collecting system. Tests, which have been described in detail in an earlier paper, had proven that two such tubes in series absorb practically all the emanation passing through them during a 20-hour run. Each set of tubes was permanently labeled and their relative absorptive powers carefully determined for the conditions under which they were to be used.

The bottle containing the radium bromide solution was so arranged that it could be heated by immersing in a solution of sodium chloride. A large spherical condenser was attached to the bottle to prevent loss of the radium bromide during the process of heating. The standard used throughout the entire series of determinations contained 6.28×10^{-10} grams of radium. Preceding each test the solution was put into the so-called " steady state " by bubbling air through the boiling solution for one hour and then through the cool solution for two hours. Our preliminary work had shown conclusively that bubbling air through the cool solution did not remove all the acculumated emanation, nor remove it as rapidly as formed even after the solution had been put in the " steady state." Under the conditions maintained throughout the tests approximately 80 per cent. of the emanation was removed from the solution. This is absolutely independent of the question of what per cent. of the total amount passing over the charcoal is absorbed. In comparative tests the only point of importance in regard to the absorption is that each branch shall absorb the same fraction of the total amount passing through it.

Testing.—The testing apparatus used was a Spindler and Hoyer aluminum-leaf electroscope with an ionization chamber attached. The aluminum leaf in these electroscopes has a fine quartz fiber attached to one edge which makes it possible to obtain very accurate readings with the aid of the reading microscope. The ionization chamber was 38 cm. high and 7.8 cm. in diameter, giving a volume of 1,820 c.c. It was provided with two outlet tubes so that the chamber could easily be exhausted and refilled with the air containing the emanation. The electroscope with the attached ionization chamber had an electrical capacity of 8.7 e.s. units, the range of the scale of 100 divisions being approximately from 368 to 302 volts. The potential gradient, therefore, was sufficient to produce saturation currents for the degree of ionization dealt with in the experiments. The natural leak was exceedingly constant and had a value of 0.016 division per minute.

The ionization chamber was permanently attached through one opening to a mercury manometer and through the other opening to a Geryk oil pump and to two aspirator bottles, all connected in parallel, so that any one could be put in direct connection with the chamber. Between the aspirators and ionization chamber were placed two small U tubes, one containing calcium chloride and the other phosphorus pentoxide, permitting all the air passing into the chamber to be thoroughly dried.

After a few preliminary experiments we adopted the following method of taking measurements on the emanation collected. The charcoal tubes were placed in a tubular electric furnace and connected in parallel to one aspirator. The tubes were heated to a bright red heat. The temperature for the different determinations was practically the same, equal currents being always passed through the electric furnace for the same length of time. The tubes were then rapidly but thoroughly flushed until the aspirator was filled down to a certain mark. In order to prevent absorption of the emanation the water in the aspirator bottle was heated by an immersed electric coil. The air containing the emanation was then passed into the ionization chamber through the calcium chloride and phosphorus pentoxide tubes, care being taken to thoroughly flush the tubes with air so that all the emanation would be carried into the ionization chamber. The chamber had been made with the necessary volume to accommodate all the gas driven off from 140 grams of charcoal with a liberal margin for flushing. The electroscope readings were always taken over practically the same region of the scale, the reading being started as nearly as possible thirty minutes after introducing the emanation into the chamber. The deflection of the aluminum leaf for the following thirty minutes was then recorded. By this method the reading was always obtained over approximately the same portion of the decay curve for radium emanation, thereby making the electroscope readings directly comparable.

AMOUNT OF RADIUM EMANATION IN THE ATMOSPHERE AT MANILA.

The theory underlying the calculations of the radium-emanation content from observations by the charcoal-absorption method has been given by several writers on the subject. If M represents the radium equivalent in grams of the emanation in one cubic meter of free air, then

$$M = \frac{M^1 \lambda T}{V} \frac{d}{d_1},$$

where M^1 is the number of grams of radium in the standard solution, λ the radioactive constant of radium, d the electroscope reading due to the emanation from V cubic meters of air, and d_1 the electroscope reading corresponding to the emanation formed by M^1 grams of radium in the time interval T.

In the deduction of the above equation it is assumed that all the accumulated emanation has been removed from the solution previous to a run, and that all the emanation formed during the time of collecting is removed from the solution and passes through the collecting system. Our preliminary experiments had shown that this assumption is not justified for the conditions of temperature, rate of flow of air stream, etc., under which our tests were made. In which case it is necessary to multiply the above equation by some factor having a value less than unity. If we represent this factor by α the equation then becomes

$$M = \frac{\alpha M^1 \lambda T}{V} \frac{d}{d_1}.$$

A long series of determinations, with conditions maintained as rigidly constant as possible, gave for this factor a value of 0.792. Extreme care was taken throughout all our tests on the emanation content to maintain conditions the same as those existing during the determination of the value of α.

Table I. gives the results of a series of observations for the period from July, 1913, to July, 1914, together with such meteorological data as is necessary to show any existing correlation. The meteorological data is taken from the reports of the Manila Observatory which is situated about 400 meters from the Bureau of Science, consequently the two sets of data practically coincide as to location. All the radioactive determinations given in Table I. were taken under identical experimental conditions. The standard solution was put into the "steady state" by bubbling air at the rate of 0.5 liter per minute through the boiling solution for one hour and then through the cool solution for two hours. At the end of the two hours the air stream was started through the collecting system, the rate of flow being maintained constant at 0.5 liter per minute. All observations extended from 1 P.M. to 9 A.M., a period of twenty hours, making the volume of air tested in every case equal to 0.6 cubic meter. As will be seen later it is extremely important that the observations should be taken over the same part of the day if the results are to have a high comparative value.

TABLE I.

Variation of the Radium Emanation Content with Meteorological Conditions.

Date.	Pressure (Mean), (Mm.)	Nature of Variation of Pressure During the Three Days.	Humidity (Mean), (%).	Wind.			Rain, 24 Hours Beginning Midnight, (Mm.).	Rain for the Three Days, (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams $\times 10^{12}$).	Weather Remarks.
				Prevailing Direction.	Total Movement, (Km.).	Total Movement During the Three Days, (Km.).				
July 8, 1913	757.94	Decreasing	80.0	WSW	267.0	922.0	....	13.3	35.8	Fair during July 8 and during day of July 9. Very heavy shower during night of 9th.
July 9, 1913	757.60		81.6	WSW	321.0		11.8			
July 10, 1913	757.47		92.9	WSW	334.0		1.5			
July 22, 1913	755.30	Variable	91.4	WSW	468.0	1381.0	28.5	45.0	20.5	Very heavy rains during the past 10 days.
July 23, 1913	753.64		89.3	WSW	564.5		14.1			
July 24, 1913	753.91		89.4	SSW	348.5		2.4			
July 27, 1913	756.90	Decreasing	88.2	WNW	218.0	1742.0	13.8	72.7	14.5	Very heavy rains during the past 18 days.
July 28, 1913	753.74		91.0	WSW	476.0		5.0			
July 29, 1913	750.80		90.1	SW	1048.0		53.9			
Aug. 3, 1913	757.80	Decreasing	86.1	SW	290.0	830.5	1.3	24.7	23.6	Heavy typhoon weather for preceding three weeks, but only partly cloudy with occasional showers beginning with Aug. 2.
Aug. 4, 1913	757.12		93.0	SW	332.0		23.0			
Aug. 5, 1913	756.36		89.7	SW	208.5		0.4			
Aug. 17, 1913	758.60	Variable	85.9	SE	109.5	367.5	9.7	54.7	39.5	
Aug. 18, 1913	759.26		87.7	Variable	94.0		1.8			
Aug. 19, 1913	757.26		86.0	SW	164.0		43.2			

TABLE I.—*Continued.*

Date.	Pressure (Mean), (Mm.).	Nature of Variation of Pressure During the Three Days.	Humidity (Mean), %	Wind.			Rain, 24 Hours Beginning Midnight, (Mm.).	Rain for the Three Days, (Mm.)	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams $\times 10^{12}$).	Weather Remarks.
				Prevailing Direction.	Total Movement (Km.).	Total Movement During the Three Days, (Km.).				
Aug. 24, 1913	757.51	Variable	88.6	Variable	246.5	979.0	16.5	29.1	19.6	Partly fair during Aug. 22 and 23. Heavy showers during night of 24th.
Aug. 25, 1913	758.77		88.8	SW	335.5		5.3			
Aug. 26, 1913	757.34		89.0	SW quad.	397.0		7.3			
Aug. 31, 1913	757.98	Decreasing	84.3	SW	224.0	652.0	19.2	25.1	49.7	Fair during the day time of Aug. 31, but heavy showers during the night.
Sept. 1, 1913	755.98		83.0	W quad.	149.0		0.8			
Sept. 2, 1913	753.53		85.9	SW	279.0		5.1			
Sept. 7, 1913	758.48	Decreasing	84.0	WSW	271.0	1472.0	....	105.8	17.3	Occasional heavy showers during the period from Sept. 4 to Sept. 8.
Sept. 8, 1913	757.74		81.2	WSW	530.0		....			
Sept. 9, 1913	756.39		88.8	SW, WSW	671.0		105.8			
Sept. 21, 1913	757.76	Increasing	82.9	W quad.	117.5	392.0	0.8	0.8	53.4	Light afternoon showers for the period from Sept. 18 to Sept. 21 inclusive.
Sept. 22, 1913	758.62		82.0	SW quad.	159.0		....			
Sept. 23, 1913	759.83		87.8	SW quad.	115.5		....			
Sept. 28, 1913	759.57	Decreasing	82.4	W quad.	136.0	390.5	....	12.0	52.0	Light showers during the preceding week with no heavy rains.
Sept. 29, 1913	759.16		84.8	W	113.0		5.1			
Sept. 30, 1913	758.46		82.4	W quad.	141.5		6.9			
Oct. 12, 1913	753.95	Variable	88.6	N quad.	124.0	1067.0	4.7	66.3	17.1	Occasional heavy showers with considerable fine drizzling rain intervening during Oct. 10 and 11.
Oct. 13, 1913	751.87		91.6	SSW	459.0		13.1			
Oct. 14, 1913	752.36		93.3	SSW	484.0		48.5			

TABLE I.—*Continued.*

Date.	Pressure (Mean), (Mm.).	Nature of Variation of Pressure During the Three Days.	Humidity (Mean), (%).	Wind.			Rain, 24 Hours Beginning Midnight, (Mm.).	Rain for the Three Days, (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams $\times 10^{12}$).	Weather Remarks.
				Prevailing Direction.	Total Movement, (Km.).	Total Movement During the Three Days, (Km.).				
Oct. 19, 1913	760.24	Variable	81.5	E quad	70.5	201.5	0.3	0.8	77.1	Only very light showers since the 14th. Fair most of the time with light winds.
Oct. 20, 1913	760.60		86.3	SW, NW	55.0		0.5			
Oct. 21, 1913	760.24		83.7	W, WSW	76.0		....			
Oct. 26, 1913	760.28	Variable	76.5	NNW, SSW	94.0	264.5	....	....	92.2	Fair for the past week with a few light showers and light winds.
Oct. 27, 1913	760.03		78.4	W	112.0		....			
Oct. 28, 1913	760.88		81.8	W quad.	58.5		....			
Nov. 2, 1913	760.35	Increasing	82.4	NW	95.0	248.5	....	7.2	49.9	Fairly heavy local showers during the past week.
Nov. 3, 1913	760.58		88.1	W quad.	81.0		4.6			
Nov. 4, 1913	760.61		93.1	NNE	77.5		2.6			
Nov. 9, 1913	760.64	Decreasing	77.5	NE	167.5	414.0	....	3.4	75.4	Considerable rain during the preceding week, but fair on the 9th.
Nov. 10, 1913	760.60		87.2	N quad.	99.0		3.4			
Nov. 11, 1913	760.59		77.6	NE, WSW	147.5		....			
Dec. 7, 1913	762.08	Variable	78.5	NE	106.5	373.0	....	2.4	59.1	Light showers on the 5th and 6th. Fair on the 7th.
Dec. 8, 1913	761.22		79.2	ENE	119.0		1.8			
Dec. 9, 1913	761.39		82.6	NNE	147.5		0.6			

TABLE I.—*Continued.*

Date.	Pressure (Mean), (Mm.).	Nature of Variation of Pressure During the Three Days.	Humidity (Mean), (%)	Wind.			Rain, 24 Hours Beginning Midnight, (Mm.).	Rain for the Three Days, (Mm.)	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams × 10^{12}).	Weather Remarks.
				Prevailing Direction.	Total Movement, (Km.)	Total Movement During the Three Days, (Km.).				
Dec. 14, 1913	760.13		77.9	NNE	171.0		....			Afternoon showers during the preceding week. Showers during night of 13th.
Dec. 15, 1913	759.85	Variable	83.3	WNW, WSW	80.0	309.0	....	9.3	137.9	
Dec. 16, 1913	760.50		89.5	Variable	58.0		9.3			
Dec. 22, 1913	760.02		79.8	WNW, SE	114.5		....			Fair during the 21st and 22nd. Cloudy during morning of 23rd.
Dec. 23, 1913	760.27	Increasing	86.3	SE	71.5	270.0	3.0	3.0	70.8	
Dec. 24, 1913	760.33		80.2	W quad.	84.0		....			
Jan. 4, 1914	764.59		74.6	E quad.	155.5		....			Fair during the four days immediately preceding.
Jan. 5, 1914	764.34	Decreasing	78.2	E, SE	188.5	538.0	....	....	89.1	
Jan. 6, 1914	764.19		76.2	SE	194.0		....			
Jan. 18, 1914	762.93		72.0	E quad.	169.0		....			Fair.
Jan. 19, 1914	761.90	Decreasing	79.1	E quad.	161.0	531.0	....	....	145.1	
Jan. 20, 1914	761.57		76.1	ESE	201.0		....			
Feb. 1, 1914	761.02		75.0	SE quad.	195.0		....			Fair.
Feb. 2, 1914	761.12	Increasing	76.3	ESE	128.0	427.0	....	....	122.4	
Feb. 3, 1914	761.66		79.2	SE	104.0		....			

TABLE I.—*Continued.*

Date.	Pressure (Mean), (Mm.).	Nature of Variation of Pressure During the Three Days.	Humidity (Mean), (%).	Wind.			Rain, 24 Hours Beginning Midnight, (Mm.).	Rain for the Three Days, (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams $\times 10^{15}$).	Weather Remarks.
				Prevailing Direction.	Total Movement, (Km.).	Total Movement During the Three Days, (Km).				
Feb. 15, 1913	763.23	Decreasing	74.2	ESE	195.5	624.5	....	....	94.1	Fairly heavy showers during the period from Feb. 13 to Feb. 15.
Feb. 16, 1914	763.09		66.4	E quad	229.5		....			
Feb. 17, 1914	762.96		70.2	ESE	199.5		....			
Mar. 8, 1914	759.23	Increasing	69.6	ESE	264.5	755.0	....	....	108.6	Exceptionally clear and warm during the last few days.
Mar. 9, 1914	759.31		70.1	ESE	228.5		....			
Mar. 10, 1914	759.71		70.6	SE	262.0		....			
Apr. 21, 1914	761.88	Decreasing	71.6	SE	218.5	610.5	....	1.5	68.9	
Apr. 22, 1914	760.51		69.6	NNE, WSW	189.0		1.5			
Apr. 23, 1914	759.87		73.4	SE	203.0		0.3			
May 6, 1914	758.36	Variable	644.	SE	206.5	630.0	....	2.0	70.1	
May 7, 1914	759.37		66.9	SE, W	226.5		....			
May 8, 914	758.96		71.5	E quad.	197.0		2.0			
May 24, 1914	758.52	Variable	74.9	WSW	137.5	499.0	....	2.3	97.4	
May 25, 1914	758.66		78.3	Variable	155.5		2.3			
May 26, 1914	757.02		78.9	WSW	206.0		....			
June 7, 1914	759.41	Decreasing	79.5	Variable	98.0	380.5	....	6.4	63.5	Very heavy shower during the early evening of the 8th.
June 8, 1914	758.97		78.6	WNW	141.0		6.4			
June 9, 1914	758.92		77.7	W	138.5		....			

TABLE I.—*Continued.*

Date.	Pressure (Mean), (Mm.).	Nature of Variation of Pressure During the Three Days.	Humidity (Mean), (%).	Wind.			Rain, 24 Hours Beginning Midnight, (Mm.).	Rain for the Three Days, (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams $\times 10^{12}$).	Weather Remarks.
				Prevailing Direction.	Total Movement, (Km.).	Total Movement During the Three Days, (Km.).				
June 21, 1914	758.66	Variable	85.0	Variable	83.0	374.0	....	....	54.5	Very heavy rain during the period from June 18 to June 21.
June 22, 1914	758.84		83.8	Variable	103.5		....			
June 23, 1914	758.82		79.5	SE	187.5		....			
July 8, 1914	755.48	Increasing	90.5	SW quad.	282.0	1288.0	21.3	22.2	19.2	Just clearing off after almost a week of typhoon weather with very heavy rain and winds. No rain during test.
July 9, 1914	756.80		84.7	WSW	327.0		0.9			
July 10, 1914	757.05		81.6	WSW	679.0		....			
								Mean	63.4	

The mean value of the radium equivalent per cubic meter of the atmosphere at Manila, as given by the 29 observations recorded in Table I., is 63.4×10^{-12} grams. If we take the mean of all our observations for Manila we obtain a value of 76.7×10^{-12} grams, which is probably nearer the true value. Any mean determined as above, however, is subject to wide fluctuations, since the variation with weather conditions is so great that a wide range of values, even of a large number of determinations, might be obtained by bunching the observations during a definite season of the year. A better idea of the average value is obtained by taking the mean of the monthly means for an entire year. In Table II. the results by months are given, the numbers in brackets in the last column indicating the number of individual observations entering into the value for each month. The mean of the monthly means has a value of 71.0×10^{-12} grams.

Table II.

Annual Variation of the Radium Emanation Content.

Month.	Pressure (Mean), (Mm.).	Humidity (Mean), %	Wind, Total Movement for Month, (Km.).	Rain, (Total), (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, Grams $\times 10^{12}$.
July, 1913.....	756.26	86.2	10,374.6	570.6	23.6 [3][1]
Aug., 1913.....	756.93	87.0	8,843.5	349.1	27.6 [3]
Sept., 1913....	757.67	85.4	8,664.5	365.5	43.1 [4]
Oct., 1913.....	758.51	83.4	4,152.0	119.7	62.1 [3]
Nov., 1913.....	761.04	81.7	3,667.5	31.1	62.7 [2]
Dec., 1913.....	761.32	80.9	4,021.0	37.8	89.3 [3]
Jan., 1914.....	763.24	76.2	4,925.5	3.5	117.1 [2]
Feb., 1914.....	762.26	73.8	5,255.5	7.3	108.3 [2]
Mar., 1914.....	760.77	68.6	6,344.0	6.1	108.6 [1]
Apr., 1914.....	760.17	70.8	5,921.0	53.4	68.9 [1]
May, 1914.....	758.42	72.6	6,137.5	84.0	83.7 [2]
June, 1914.....	757.62	81.7	6,714.0	367.9	59.0 [2]
July, 1914.....					19.2 [1]
Mean of monthly means.................................					71.0

The following average results have been obtained for the radium-emanation content by Eve[2] at Montreal, Satterly[3] at Cambridge, and Ashman[4] at Chicago:

Eve....................	60×10^{-12} gram Ra. per cubic meter.
Satterly................	105×10^{-12} gram Ra. per cubic meter.
Ashman................	96×10^{-12} gram Ra. per cubic meter.

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[1] Number in bracket shows the number of observations entering into the monthly mean.

[2] Phil. Mag., *16*, 622, 1908.

[3] Am. Journ. Sci., 119, 1908.

[4] Phil. Mag., *20*, 1, 1910.

Eve and Satterly used the charcoal-absorption method; Ashman the condensation method. Eve's value is the mean of the monthly means for a period from July to April, Satterly's value is the mean of individual observations taken during the months of March to August, inclusive, while Ashman's is the mean of six determinations, the time of year not specified.

In comparing our results with those of Eve and Satterly it should be remembered that they both assumed that all the emanation was obtained from their standard by bubbling air through the cool solution, and consequently did not use in their calculations any factor corresponding to α. If their results are subject to a correction of approximately the value which we found for α, then our mean is considerably greater than that of Eve for Montreal and slightly less than that of Satterly for Cambridge. No great importance is here attached to the fact that our mean value for Manila seems to be nearer to that for Cambridge than Montreal, except in so far as it may throw light on the question as to what extent the value of the emanation content is dependent on the distance that the air tested has traveled over land or water.

Variation of the Emanation Content with Meteorological Conditions.

From a study of the individual observations of Table I. a distinct correlation is observed between the values of the emanation content and certain of the meteorological factors. For each observation of the emanation content we have given the meteorological data for three days, including the two days during which the observation was taken and the preceding day. That a distinct relation exists between the emanation content, the rainfall and the wind movement is readily seen. In every case a period of heavy rains accompanied by high winds corresponds to a low value of the radium-emanation content, while fair weather with light winds gives correspondingly high values. A good idea of the magnitude of this variation is obtained from the ratio of the maximum to the minimum, which has approximately the value of ten to one. Since in Manila the temperature is fairly constant throughout the year the variations in rainfall and wind movement must necessarily be the chief causes of the wide difference in the values of the atmospheric radioactivity. Which one of the two factors is the more important is somewhat doubtful, since they are generally so correlated that it is difficult to determine exactly what part of the total effect is due to either one.

Not only is there a close relation between the emanation content, the rainfall and the wind movement for the individual observations, but also for the means for the months, as shown in Table II. Taken in conjunction with Table I. it is seen that the observations scattered throughout the month are fairly typical for the entire period. This is especially true for the months in which three or more observations were taken. It is to be regretted that during certain months the rush of other work prevented our taking as large a number of observations as we should have liked. The month of January gives the highest value for the activity, the minimum value for the rainfall, and a low value for the wind movement. July shows the lowest activity, the maximum rainfall and the highest wind movement. A similar relation exists for almost every month of the year. The month of June from Table II. would appear to be an exception, but by referring to Table I. it is seen that the two observations for the month were taken at periods of very little rainfall and comparatively low wind movement, and consequently are not typical of the entire month as far as rain and wind is concerned.

One other factor, namely the direction of the wind, may possibly have an appreciable effect on the value of the emanation content. The location of Manila is such that for the greater part of the year the prevailing wind is from off the sea. Even those which are apparently land breezes, with the exception of those from the northeast quadrant, have at the most passed but a comparatively short distance over land. During the rainy season the prevailing winds are westerly and the radium-emanation content is low, but just as soon as the rainfall and the wind movement decrease the radioactivity increases, even though the direction of the wind remains the same. Certain observations, however, seem to indicate that the highest values are obtained on days when the air currents are from the land, but the results are so uncertain as to practically prohibit the drawing of any definite conclusions. A more detailed discussion of this point will be given in connection with certain observations in which the factor of rainfall is absent.

DIURNAL VARIATION OF THE RADIUM-EMANATION CONTENT OF THE ATMOSPHERE.

In our earlier work on the subject we had noticed that there seemed to be a large variation between consecutive observations taken over different parts of the day. No definite attempt had been made, however, to determine accurately the diurnal variation.

Several observers have investigated the question of the daily variation of the radioactivity of the atmosphere by the active-deposit method. Simpson[1] in Lapland made four determinations a day (3–5 A.M., 10–12

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[1] Phil. Trans. Roy. Soc., A-V, CCV., 61, 1905.

A.M., 3–5 P.M., and 8.30–10.30 P.M.) for a period of almost a year. His results showed a maximum for the early morning hours and a minimum about noon, the ratio of the maximum to the minimum being approximately 3 to 1. Gockel[1] at Freiburg likewise found an increase in the early morning and at times a depression about noon. Blackwood[2] at Manila found a maximum about 4 A.M. and a minimum around 6 P.M., the ratio of the means being approximately seven to one. These three observers obtained the active deposit on a negatively charged wire stretched horizontally in free air.

In order to eliminate the variable factor of wind force, Dike[3] used a modification of the above method. The air to be tested was drawn at a definite rate through a wooden pipe over one end of which was fitted a piece of wire gauze. The gauze was well insulated and charged to a high negative potential. The radioactive substances were collected on the gauze and tested in the usual manner. As a mean of six sets of observations, each extending over approximately twenty-four hours, a decided maximum was found in the early morning which decreased to a strong minimum during the early evening. The maximum had a value approximately eighteen times the minimum.

Hess[4] using a method somewhat similar to Dike's found an early morning maximum which decreased to a minimum about 11.30 A.M. rising again to a secondary maximum at 4 P.M. and then rapidly falling to a decided minimum around 6 P.M. The greatest variation found was only about 20 per cent. from the mean value.

From the work of these observers it seems quite certain that the emanation content is considerably greater in the early morning hours than during the late afternoon, even for widely scattered points on the earth's surface. The active-deposit method fails, however, to throw much light on the cause of this variation. Simpson drew the following conclusions from his results:

1. For the whole year temperature has a marked effect, but very little effect during any one month.

2. The radioactivity increases with increase in the humidity and decreases with decreasing humidity.

3. The radioactivity is greater with a falling barometer than with a rising barometer, although the activity is not necessarily higher with a low barometer than with a high one.

4. The radioactivity is greater for winds from the land than for winds from the sea.

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[1] Phys. Zeit., 5, 591, 1904.

[2] Phil. Journ. Sci., IX–A, No. 4, 1914.

[3] Terr. Mag., 125, 1906–07.

[4] Sitz. d. k. Ak. d. Wiss., *119*, 145, 1910.

Hess likewise concluded that a decrease in pressure was accompanied by an increase in the active deposit, and vice versa.

The question of whether all these factors directly affect the emanation content or whether certain of them cause merely a variation in the amount of active deposit collected led us to take some observations by the charcoal-absorption method. Since the object of these tests was to determine the causes rather than the nature of the diurnal variation no attempt was made to take observations of extremely short duration.

The first series of tests were taken with the object of determining the relation existing between the emanation content for day and night periods. The day tests extended in every case from 6.30 A.M. to 6.30 P.M., and the night from 6.30 P.M. to 6.30 A.M. The corresponding day and night observations were always made within the 24 hour period in order that the individual readings might have a direct comparative value. The results are given in Table III. With one exception all the night obser-

TABLE III.

Diurnal Variation of the Radium Emanation Content.

Day determinations. Time.—6.30 A.M. to 6.30 P.M.

Night Determinations. Time.—6.30 P.M. to 6.30 A.M.

	Date.	Pressure Variation.	Humidity (Mean), (%).	Wind.		Rain for 12 Hours, (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams × 10^{15}).
				Prevailing Direction.	Total Movement for the 12 Hours, (Km.).		
Day Determinations	Dec. 29, 1913.....	Variable	67.5	Variable	97.0	....	68.3
	Jan. 2, 1914......	"	65.5	N	125.5	....	51.8
	Jan. 12, 1914.....	"	70.6	Variable	118.5	....	66.1
	Jan. 14, 1914.....	"	76.4	N	85.0	....	59.5
	Jan. 16, 1914.....	"	75.4	Variable	65.0	....	36.2
	Jan. 27, 1914.....	"	63.4	Variable	127.5	....	68.0
	Jan. 29, 1914.....	"	68.2	Variable	99.0	....	68.0
	Feb. 24, 1914.....	"	68.4	W. quad.	118.0	....	85.5
	Mean..................................				104.4	....	62.9
Night Determinations	Dec. 29–30, 1913..	Variable	80.8	NE	75.0	....	66.9
	Jan. 2–3, 1914....	"	80.9	N	27.5	....	52.4
	Jan. 12–13, 1914..	"	89.1	Calm	29.5	....	165.0
	Jan. 13–14, 1914..	"	85.1	Calm	40.5	....	111.3
	Jan. 15–16, 1914..	"	86.0	Calm	21.0	....	133.8
	Jan. 26–27, 1914..	"	79.0	ESE	65.0	....	108.3
	Jan. 28–29, 1914..	"	78.2	ESE, Calm	48.0	....	174.9
	Feb. 24–25, 1914..	"	84.0	SE	32.0	....	173.5
	Mean..................................				41.1	....	123.3

Table IV.

Diurnal Variation of the Radium Emanation Content.

Day Determinations. Time.—11 A.M. to 5 P.M.

Night Determinations. Time.—11 P.M. to 5 A.M.

	Date.	Pressure Variation.	Humidity (Mean), (%).	Wind.		Rain for 6 Hours, (Mm.).	Radium Emanation per Cu. M. Expressed in its Radium Equivalent, (Grams $\times 10^{18}$).
				Prevailing Direction.	Total Movement for the 6 Hours, (Km.).		
Day	Feb. 27, 1914.....	Decreasing	57.9	E. quad.	98.0	.....	45.8
	Mar. 25, 1914....	Decreasing	42.9	Variable	117.5	.....	26.1
	Mar. 30, 1914....	Decreasing	53.3	WSW, SE	73.5	.....	34.1
	Mean....................................				96.3	.....	35.3
Night	Feb. 26–27, 1914..	Decreasing	90.0	Calm	12.5	.....	132.0
	Mar. 24–25, 1914.	Decreasing	78.0	Calm	19.0	.....	116.7
	Mar. 30–31, 1914.	Variable	81.0	ESE, Calm	8.0	.....	104.5
	Mean....................................				13.2	.....	117.7

vations gave higher values than those for the day. The ratio of the mean value for the night to the mean for the day is 1.95.

A few observations were also taken in which the time of collecting was shortened to 6 hours, the results of which are given in Table IV. Since all the observers using the active-deposit method seem to agree that the radioactivity reaches a maximum in the early morning hours and falls to a minimum some time during the afternoon we chose for our 6-hour observations the intervals from 11 A.M. to 5 P.M., and 11 P.M. to 5 A.M., respectively. As in the 12-hour observations corresponding day and night tests were always taken within the 24-hour period. Again it is seen that the night values are all consistently higher than the day values, the ratio of the mean for the night to the mean for the day being 3.31.

From the above results it appears quite evident that there is a decided daily variation of the emanation content of the atmosphere at Manila. Moreover, the variation found by the charcoal-absorption method seems to be in good agreement with the results obtained by the active-deposit method. This would seem to indicate that the active-deposit method is fairly reliable for determinations of the variation at any given locality. That observations taken at widely different altitudes would possess the same comparative value does not necessarily follow, since changes in pressure, nucleation, etc., would in that case introduce undetermined factors. The charcoal-absorption method, moreover, lends itself much more readily to a study of the causes of the existing variation.

The data in Tables III. and IV. show quite conclusively the effect of the total wind movement. The observations were all taken during the dry season and the factor of rainfall is entirely eliminated. Without exception the total wind movement for the day observations was considerably greater than for the corresponding night determinations. For the 12-hour tests the total wind movement for the day is 2.54 times that for the night. This is approximately of the same value as the ratio for the radium-emanation content. The fact that the two relations happen to have nearly the same numerical value has probably no direct significance, but it certainly shows that the question of atmospheric circulation, independent of rainfall, has a very decided influence on the variation of the emanation content. For the 6-hour tests the total wind movement for the day is approximately 7.32 times that for the night, or roughly twice the ratio for the emanation content. From these two series of observations we are able to obtain a fair idea concerning the extent to which the high wind movement is responsible for the decrease of the radioactivity of the air. A study of Table I. in the light of the above results leads to the conclusion that at Manila the fluctuation in the total wind movement is probably responsible for almost one half of the observed variation of the radium-emanation content.

It was also thought probable that the direction of the wind during the different parts of the day might have considerable influence on the above variation. A careful study of the hourly data for the periods of observation fails to show, however, any definite relation. Consequently, we are led to the conclusion that for Manila the important factor, in regard to the wind, is not whether it has passed for a long distance over land or sea, but almost entirely one of rapidity of circulation. That the same relation would be found to exist for a point differently situated with regard to water and land does not necessarily follow.

If the circulation of the air rather than its direction is the important question then evidently the decrease of the emanation content due to the wind may be explained as due almost entirely to the mixing of air of low and high emanation content. Moreover, it seems as if all air in rapid circulation is such a mixture, regardless of whether it has passed for a long distance over water or not. This is easily explained if we assume that the air in rapid circulation over land is a mixture of air of high and low altitude, since without doubt the emanation content of the atmosphere decreases with altitude. Only when the air is very still does the amount of emanation it contains begin to approach that exhaled from the ground for the given locality. We are perfectly cognizant that the above explanation may be applicable only to our particular location.

Manila is so situated that practically all land breezes have passed within a short distance over low mountain ranges, which will tend to give a mixture such as assumed above.

The correlation between the radioactive constituents of the atmosphere and the temperature, humidity, and pressure has been the subject of much investigation, but the results are decidedly discordant. For this reason we thought it advisable to include in our tables the data showing the variation in humidity and barometric pressure. The temperature for Manila is so nearly constant for the year that it has been omitted. A careful study of all our results fails to give any convincing evidence that the emanation content is directly dependent to any appreciable extent on either the humidity or the pressure. In the course of this study we plotted the pressure-time curves for the results given in Tables III. and IV., but were absolutely unable to discover any definite relation for either an increasing or decreasing pressure. Since most of the previous investigations on this phase of the question have been made by the active-deposit method it seems probable that whatever relation was found to exist was due to a variation of the collecting distance rather than to any actual change in the emanation content. That the results obtained by the active-deposit method are influenced by the humidity of the air has been shown by the work of Simpson, Blackwood and others.

Supply of Radium to the Air from Soil Gas.

Exhalation.—It has been fairly conclusively shown that the earth's crust is the source of the radioactive substances in the atmosphere. A large amount of work by numerous observers has also demonstrated that the radioactive substances are fairly uniformly distributed throughout the surface of the earth. Consequently it is to be expected that more or less emanation is being exhaled from the earth's surface at every point. That the rate of exhalation will vary with the physical and chemical conditions of the surface is to be expected. In order to determine the effect of weather conditions on the rate of exhalation we made a few tests on the emanation exhaled from the surface of the ground at Manila. As far as we have been able to learn the only direct tests made on the exhalation are those of Joly and Smyth at Dublin. Joly and Smyth,[1] working together, made determinations at two different locations, obtaining as mean values 839×10^{-12} and $4{,}087 \times 10^{-12}$ curie per square meter respectively. Smyth,[2] independently, obtained as a mean of 98 observations, taken at a point about 12 meters from the Geological Laboratory of Trinity College, a value of $2{,}637 \times 10^{-12}$ curie.

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[1] Proc. Roy. Dublin Soc., XIII., 148, 1911.

[2] Phil. Mag., 24, 632, 1912.

In order to obtain tests on the emanation exhaled a collecting system somewhat similar to that used by Joly and Smyth was devised. The collector consisted of a cylindrical vessel, 20 cm. in diameter and about 30 cm. deep, open at one end and closed, with the exception of a 4 cm. neck, at the other. The open neck was fitted with a rubber stopper from which portions had been cut to allow the inflow of air. Through the stopper and along the axis of the cylinder was passed a brass tube which supported at its lower end a brass disk, 19.4 cm. in diameter. This disk hung about 1.5 cm. above the open end of the cylindrical vessel. When a test was to be made the collector was placed on a level portion of the campus about 7 meters from the north wall of the Physics Laboratory, and pressed very lightly into the ground. The brass tube was then connected, through the charcoal tubes, to a motor driven pump. When the pump was started the air was drawn down into the cylinder through the openings in the rubber stopper, passing over the edges of the brass disk and along the surface of the ground and then up through the brass tube to the charcoal tubes. It was assumed that by this means practically all the emanation exhaled from the confined portion of the surface would be swept into the collector and carried to the charcoal (see Fig. 1).

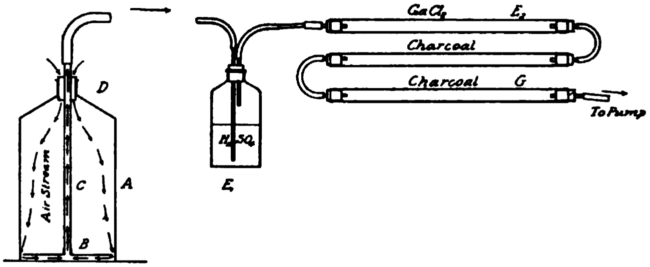

Fig. 1.

A, brass cylinder; *B*, brass disk; *C*, brass tube; *D*, rubber stopper with portions cut out; E_1 and E_2, drying system; *G*, coconut charcoal tubes.

The rate of flow of the air stream was measured by a gauge and was kept fairly constant at about 0.5 liter per minute, the period of collecting being generally one hour. Two charcoal tubes, each containing 70 grams of charcoal, were connected in series. Judging from our preliminary experiments two such tubes should absorb practically all the radium emanation passing through them during a test. The emanation collected in the charcoal was tested in the usual manner.

The results are given in Table V. and are expressed in terms of the radium equivalent of the emanation exhaled in one hour from a surface of one square meter. Although the number of our observations is limited,

TABLE V.

Radium Emanation Exhaled from the Ground.

Date.	Radium Emanation in Air Exhaled per Hour from 1 Square Meter of Ground Surface Expressed in its Radium Equivalent, Grams $\times 10^{12}$.	Weather Remarks.
June 18, 1914..	1642.0	Dry, except for very light showers during the past two weeks.
June 20, 1914..	785.2	Fairly heavy rain during day and night of June 19th. Light rain at intervals during morning of 20th. Light rain during time of collecting.
July 9, 1914...	694.0	Heavy rain and high winds for the last 6 days. A very heavy shower fell for about 15 minutes during the time of collecting.
Aug. 18, 1914..	1122.3	Fair for last three days. A few light showers during the nights. No real heavy rains for almost three weeks.

nevertheless, they show quite plainly the relation of the exhalation for the dry and wet seasons. The observation of June 18 was taken just before the breaking up of the dry season, while that of July 9 followed a week of exceptionally heavy rain. The result of June 18 is 2.37 times that of July 9. This shows approximately to what extent the radioactivity of the air is apt to vary due to rain alone. This is absolutely independent of the question whether rain falling through the air carries down with it any of the emanation. Whether the variations in the wind force effects the rate of exhalation from the ground is still an open question. Since in the above tests the air current remains constant, they throw no light on this phase of the question. The number of our tests is not sufficient to give more than a general idea of the mean value of the radium emanation exhaled at Manila, although our results are in good agreement with those of Joly and Smyth. Without doubt the months of the dry season would show a value as great or greater than that of June 18.

Emanation Content of Soil Gas.—Since the effect of rain is to decrease the rate at which the radioactive emanations are exhaled from the surface of the ground there should be a corresponding increase in the emanation content of the soil gas below the surface. Joly and Smyth found this to be the case for their observations at Dublin, but Satterly[1] failed to discover any correlation between the fluctuations of the emanation content and weather conditions, except for one pipe which always gave low results after rain and high results in fine weather. It was this apparent discrepancy in the results of experimenters working under practically

[1] Proc. Cambridge Phil. Soc., *16*, 514, 1912.

identical conditions which led us to extend our work so as to include a few observations on soil gas.

To obtain the ground air we made three pipes of brass tubing, 9 mm. inside diameter, and 130 cm., 75 cm., and 37 cm. in length. One end of each pipe was fitted with a pointed brass plug. For a length of about 6 cm. from the closed end, holes, sloping slightly downward, were drilled. The pipes were then driven into the ground at a distance of about two meters from a window of the Physics Laboratory to such depths that the mean positions of the portion in which the holes were drilled were approximately 120, 70, and 30 cm., respectively, below the surface of the ground.

The air to be tested was pumped directly into an accurately calibrated gas bottle of one-liter capacity, care being taken in every case to pump out all the air in the pipes previous to taking an observation. Connected in parallel with the gas bottle was a manometer by means of which we could be absolutely certain that the bottle was always filled with gas at atmospheric pressure. After a sufficient time had elapsed to permit the decay of the thorium emanation the air collected was passed into the ionization chamber and tested in the usual manner.

TABLE VI.

Radium Emanation in Ground Air.

Date.	Radium Emanation per Cubic Meter of Ground Air Expressed in its Radium Equivalent, (Grams × 10^{15}).			Weather Remarks.
	Pipe No. 1, Depth 30 Cms.	Pipe No. 2, Depth 70 Cms.	Pipe No. 3, Depth 120 Cms.	
June 15, 1914..			311.5	Dry, except for very light showers, during the period from June 5 to June 15.
June 16, 1914..	32.9	209.1		Generally fair with no rain.
June 17, 1914..	29.4	208.1	269.7	Continued fair weather.
June 19, 1914..	69.5	244.2	284.1	Fairly heavy rain accompanied by high wind during the night of June 18 and continuing during June 19.
June 22, 1914..	44.0	261.6	319.0	Heavy rains up till afternoon of June 20, followed by light showers during June 21 and June 22.
June 24, 1914..	40.7	249.2	314.0	Fair during the last two days. A fairly heavy shower for about 15 minutes when collecting air from Pipe No. 3.
July 14, 1914..	64.0	297.8	321.5	Very heavy rains and high winds during the period from July 4 to July 10 Intervening four days partially fair.
Aug. 19, 1914..	35.1	274.2	314.0	Fair the last four days. A few light showers during the nights. No real heavy rains for almost three weeks.

The results of the observations are given in Table VI. Generally about two hours elapsed between the different observations taken on any given day. It is seen that the values for the 30 cm. pipe fluctuate decidedly with the amount of rainfall, being greater immediately after a period of heavy rains. The 70 cm. pipe shows a slight increase for the rainy weather while the 120 cm. pipe is but little affected. All the results tend to show, however, that the effect of rain is to stop up the soil capillaries, thus retarding the rate of escape of the ground gas, and thereby permitting the emanation in the soil air to approach nearer its equilibrium value.

Summary of Results.

1. The variation of the amount of radium emanation in the atmosphere at Manila has been determined for a period of about thirteen months. The annual and diurnal variation has been studied in connection with the principal meteorological factors. The effect of weather conditions on the rate at which radium emanation is exhaled from the surface of the ground has been investigated with the object of determining its connection with the emanation content of the atmosphere. The relation between the rate of exhalation and the radioactivity of soil gas at different depths has also been investigated.

2. The variation of the radium-emanation content of the atmosphere has been found to follow quite closely the variations in rainfall and wind movement. The ratio of the maximum to the minimum for the year was found to be approximately as 10 to 1. The mean of the monthly means gives for the radium equivalent of the emanation per cubic meter of air a value of 71.0×10^{-12} grams. The month of January shows the highest monthly mean for the radium-emanation content, the minimum value for the rainfall, and a low value for the total wind movement. The month of July gives the lowest monthly mean for the emanation content, the maximum value for the rainfall, and the highest total wind movement. Every other month of the year shows a very similar relation. No direct connection has been discovered between the emanation content and atmospheric pressure or humidity. The effect of the direction of the wind seems at best very indefinite.

3. A decided diurnal variation has been found to exist, the emanation content being considerably greater during the night than during the day. Observations for the interval from 11 P.M. to 5 A.M. gave a mean value 3.31 times greater than the mean value for the interval from 11 A.M. to 5 P.M. This variation has been found to be closely related to the variation in the total wind movement during the period, a high value of the wind movement corresponding to a low value of the emanation content.

4. The rate at which radium emanation is exhaled from the surface of the ground shows a decided decrease after periods of heavy rain. This decrease has been found in some cases to be almost 60 per cent. of the rate of exhalation for fair weather.

5. The radium-emanation content of soil gas has been determined for depths of 30, 70, and 120 cm., respectively, and the variation with weather conditions studied. The variation in the radioactivity of the gas from the 30 cm. pipe was found to follow closely the variation in the emanation exhaled, a decrease in the exhalation resulting in a corresponding increase in the emanation content of the ground gas. The 70 cm. and 120 cm. pipes showed only slight variations with the weather conditions. The average value of the emanation content for the gas collected from the 120 cm. pipe was found to be 304.5×10^{-12} grams per liter, or over 4,000 times the mean value for atmospheric air. The mean value for the 30 cm. pipe was only about one seventh that for the 120 cm. pipe.

THE CATHODE FALL IN GASES.

By C. A. Skinner.

THIS article is the result of an attempt to develop a theory of the so-called cathode fall in gases, at least to an extent sufficient to suggest intelligent experimental investigation. From the nature of the problem the theory as developed is rather crude. Since, however, it has led to the discovery of certain interesting and quite general relations between the magnitudes involved, which corroborate in part the theoretical deductions, its presentation seemed a logical introduction to these experimental results and necessary to their interpretation.

The theory is based on the generally accepted principles governing ionization by impact and the mobility of the ions, on the one hand, combined on the other with the suggestion made by the writer that the accumulation of the positive ions at the cathode face arises from an elastic rebound of these ions when they impinge on the cathode.[1]

For the sake of clearness we will give first a brief summary of the principal features connected with this cathode fall. Take for example a cylindrical glass tube containing gas at a pressure such that a glow current can be maintained between two disk electrodes placed one in each end of the tube and perpendicular to its axis. For simplicity let the current be confined to the front face of the cathode.

Potential measurements show an extremely low gradient in the negative glow as compared with that at any other portion of the conducting gas. Passing toward the cathode from this region of minimum gradient, one finds that the gradient begins to increase relatively rapidly at a certain point and climbs gradually higher as the cathode is approached.[2]

The negative glow is marked usually by its hazy blue color. The point where the abrupt rise in the gradient begins, is, especially at the higher gas pressures or higher current densities, very distinctly marked as the outer boundary of a bright luminous striation (much whiter than the rest of the negative glow). Towards the cathode this bright striation shades off rapidly to darkness, in the so-called cathode dark space, un-

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[1] C. A. Skinner, Phil. Mag., VI., Vol. 4, p. 490, 1902.

[2] This characterization does not include the cases at very low gas pressure in which Graham (Ann. d. Physik, 64, p. 49) observed the gradient to climb in a sinuous manner in passing from the negative glow to the cathode.

accompanied by any correspondingly marked change in the gradient except its gradually increasing magnitude. On the face of the cathode is again a very bright and relatively thin striation.

The potential difference between the cathode and the very low gradient region of the negative glow is known as the "cathode fall." This cathode fall is remarkable in that its magnitude is the same over a wide range of gas pressures, provided the conditions admit of an automatic adjustment of the cathode current density to its so-called normal value.[1] The cathode fall thus obtained is known as the "normal cathode fall."

The potential difference between the cathode and a very fine wire placed only a fraction of a millimeter from it, is, in hydrogen, one half or more of the cathode fall; in nitrogen, it may be a large part of the fall.

If, by means of auxiliary electrodes connected with a constant potential source, one sends a current across the main stream, this cross-current is found to be distinctly larger in the negative glow than at any other part. It decreases especially rapidly as one moves from the negative glow to the cathode. This fact, together with the results of various other experiments which point to the same conclusion, has led to the generally accepted view that the negative glow is very largely the source of the ions which carry the current between that point and the cathode. Thus we have on the cathode side of the negative glow the current carried very largely by the less mobile positive ions moving to the cathode, while to the anode side we have the more mobile electrons. Consequently, on the cathode side we have a greater density of charge, hence a more rapidly increasing potential gradient than on the anode side.

The relatively large potential difference between the cathode and the gas immediately adjacent necessitates the assumption of a greatly decreased mobility of the ions at this point. Many investigators explain this decreased mobility by assuming the existence of a high resistance film on the face of the cathode.

We are interested here however in deducing the results which should arise if the impinging positive ions rebound from the cathode with a definite fraction of their incident energy and only communicate their charge to the cathode (or receive a neutralizing charge from it) when they finally come to rest at its surface. A still more acceptable view would allow for a part of the kinetic energy of the rebounding ion being absorbed by friction in the gas, but the theoretical application of this view appears impossible.

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[1] At low gas pressures the minimum cathode fall rises distinctly above this "normal" value, as repeatedly observed during the present investigation. The phenomenon of an automatic adjustment of current density also disappears.

Theory.

Fall of Potential in the Region between the Negative Glow and Apparent Cathode Film.—Consider a plane cathode perpendicular to the x-axis having a discharge area sufficiently large so that the equipotential surfaces between it and the negative glow are plane and parallel—also the current density uniform.

Throughout that region in which the fall of potential per mean free path, $\bar{\lambda}$, of the electron, is greater than the ionizing potential, we should have, on the average, each electron which leaves the cathode resulting in two electrons at the end of the first mean free path; four at the end of the second; eight, at the third; and so on. With a current density of electrons leaving the cathode equal to $\bar{j}_k$, there should be under a stationary current, at a distance from the cathode $(x_k - x)$, a current density of electrons

$$\bar{j} = \bar{j}_k \cdot 2^{\left(\frac{x_k - x}{\bar{\lambda}}\right)} \tag{1}$$

provided the potential gradient is large enough to cause ionization to take place at each mean free path; and provided, as we may safely assume with such high field strength, the disappearance of electrons by recombination is negligible.[1] Beyond this region of ionization at every mean free path we are under the necessity of assuming another law of ionization. For reasons which will become evident we have assumed the upper limit, namely: that, in the remainder of the path to the point of minimum gradient in the negative glow, ionization occurs on the average whenever an electron traverses a distance over which the fall of potential is equal to the ionizing potential. This is the maximum ionization which could occur under the most favorable conditions of perfectly elastic impact and no recombination.

Between the position x_a where the electrons cease to ionize at each impact and that of the minimum gradient in the negative glow x_0, the number of electrons doubles on moving through the ionizing potential ϵ. Then, since from (1) the negative current density at x_a is

$$\bar{j}_k \cdot 2^{\left(\frac{x_k - x_a}{\bar{\lambda}}\right)}$$

that at any potential V between x_a and x_0 is

$$\bar{j} = \bar{j}_k \cdot 2^{\left(\frac{x_k - x_a}{\bar{\lambda}} + \frac{V - V_a}{\epsilon}\right)} \tag{2}$$

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[1] From our measurements of the gradient in hydrogen and Franck and Hertz's value (Verh. d. D. Phys. Ges., *15*, p. 34, 1913) of 11 volts for its ionizing potential, this region of ionization at every mean free path extends nearly to the outer boundary of the cathode dark space.

and the positive current density at the same point necessarily

$$\overset{+}{j} = j - \overset{-}{j}_k \cdot 2^{\left(\frac{x_k - x_a}{\bar{\lambda}} + \frac{V - V_a}{\epsilon}\right)} \tag{3}$$

where j, the total current density, is the same at all parts of the path. We shall use these two equations for obtaining the desired relation between potential and current density, but first it is necessary to obtain $\overset{-}{j}$, $\overset{+}{j}$ and $\overset{-}{j}_k$ in terms of j.

At the position x_0, having potential V_0, (2) gives

$$\overset{-}{j}_0 = \overset{-}{j}_k \cdot 2^{\left(\frac{x_k - x_a}{\bar{\lambda}} + \frac{V_0 - V_a}{\epsilon}\right)}. \tag{4}$$

Poisson's equation,

$$\frac{d^2V}{dx^2} + \frac{d^2V}{dy^2} + \frac{d^2V}{dz^2} = -4\pi\rho,$$

(ρ being the volume density of the charge at the point considered)—applied to the present case, where the equipotential surfaces are plane and parallel, gives

$$\frac{d^2V}{dx^2} = -4\pi\rho. \tag{5}$$

At x_0, dV/dx being a minimum, we have from this equation

$$\rho_0 = 0.$$

That is

$$\overset{+}{\rho}_0 + \overset{-}{\rho}_0 = 0. \tag{6}$$

But

$$\overset{+}{\rho}_0 = -\frac{\overset{+}{j}_0}{\overset{+}{\mu}\left(\frac{dV}{dx}\right)_0} \quad \text{and} \quad \overset{-}{\rho}_0 = \frac{\overset{-}{j}_0}{\overset{-}{\mu}\left(\frac{dV}{dx}\right)_0}, \tag{7}$$

where $\overset{+}{\mu}$ and $\overset{-}{\mu}$ are the mobilities (velocity in unit field) of the positive and negative ions respectively, hence $-\overset{+}{\mu}(dV/dx)_0$ and $\overset{-}{\mu}(dV/dx)_0$ respectively their velocities at x_0.[1] Substituting from (7) in (6) and applying also the necessary condition that

$$\overset{+}{j}_0 + \overset{-}{j}_0 = j$$

we obtain

$$\overset{-}{j}_0 = \frac{\overset{-}{\mu}}{\overset{+}{\mu} + \overset{-}{\mu}} j. \tag{8}$$

Using this last equation to obtain the value of $\overset{-}{j}_k$ from (4) and then substituting that value in (2) and (3)

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[1] The signs as used here enable both $\overset{-}{j}_0$ and $\overset{-}{\mu}$ to be treated as positive quantities, $(dV/dx)_0$ being negative.

$$\overset{-}{j} = \frac{\overset{-}{\mu} + \overset{+}{\mu}}{\overset{-}{\mu}} \cdot j \cdot 2^{-((V_0-V)/\epsilon)},$$

$$\overset{+}{j} = j\left\{1 - \frac{\overset{-}{\mu}}{\overset{-}{\mu} + \overset{+}{\mu}} 2^{-((V_0-V)/\epsilon)}\right\}. \tag{9}$$

We now proceed to obtain the desired solution. At the position x, having a potential V, equation (5) gives

$$\begin{aligned}\frac{d^2V}{dx^2} &= -4\pi\rho \\ &= -4\pi(\overset{+}{\rho} + \overset{-}{\rho}) \\ &= 4\pi\left(\frac{\overset{+}{j}}{\overset{+}{\mu}\dfrac{dV}{dx}} - \frac{\overset{-}{j}}{\overset{-}{\mu}\dfrac{dV}{dx}}\right).\end{aligned} \tag{10}$$

Substituting now in 10 the values of $\overset{-}{j}$ and $\overset{+}{j}$ as given in 9 we obtain the differential equation for the region comprised between the point x_0 of minimum gradient and x_a where the ions cease to ionize at every mean free path:

$$\frac{dV}{dx}\frac{d^2V}{dx^2} = \frac{4\pi j}{\overset{+}{\mu}}\left\{1 - 2^{-((V_0-V)/\epsilon)}\right\}. \tag{11}$$

Integrating this

$$\frac{dV}{dx} = -\left\{\frac{12\pi j}{\overset{+}{\mu}}\left[(V_0 - V) - \epsilon\left(1 - 2^{-((V_0-V)/\epsilon)}\right)\right]\right\}^{1/3}, \tag{12}$$

where the condition is introduced that, as shown by the experiment, the gradient dV/dx is practically zero at the position x_0, in the negative glow. A general solution of this equation for V is impossible. Since however the exponential term diminishes rapidly with increasing values of $[(V_0 - V)/\epsilon]$ one may find by trial a value of $(V_0 - V) = q$ such that, if the upper limit of $(V_0 - V)$ be sufficiently high,

$$\int_{V_0}^{V}\frac{dV}{dx}dx = \left(\frac{12\pi j}{\overset{+}{\mu}}\right)^{1/3}\left\{\int_{V_0}^{V_0-q}(V_0 - V)^{1/3}dx + \int_{V_0-q}^{V}(V_0 - V - \epsilon)^{1/3}dx\right\}. \tag{13}$$

The following less accurate approximation, however, lends itself more readily to an experimental test of the theory.

From (12) it is obvious that

$$\frac{d}{dx}(V_0 - V) < \left(\frac{12\pi j}{\overset{+}{\mu}}\right)^{1/3}(V_0 - V)^{1/3},$$

also (14)

$$\frac{d}{dx}(V_0 - V) > \left(\frac{12\pi j}{\overset{+}{\mu}}\right)^{1/3}(V_0 - V - \epsilon)^{1/3}.$$

Solving these

$$V_0 - V < \left\{\left(\frac{16\pi j}{\overset{+}{\mu}}\right)^{1/3}(x - x_0)\right\}^{3/2} \tag{15}$$

and

$$V_0 - V > \left\{\left(\frac{16}{9}\cdot\frac{\pi j}{\overset{+}{\mu}}\right)^{1/3}(x - x_0) - \epsilon^{2/3}\right\}^{3/2} + \epsilon \tag{16}$$

for the region between x_0 and x_a.

The right hand side of (15) may be shown to be the value of $(V_0 - V)$ in case x_0 were the sole source of the ions. Then (15) holds for the minimum possible (zero) ionization in the region considered. Hence it holds also for the entire region between negative glow and apparent cathode film.

On the other hand (16) holds, as already stated, for the maximum possible ionization in the region between x_0 and x_a. This same law of ionization, if applied in the region between x_a and the apparent cathode film, would produce a larger ionization than that at every mean free path. It follows then that (16) also holds between the negative glow and the apparent cathode film.

Letting then x_b locate the outer edge of the apparent cathode film and V_b its potential

$$\begin{aligned} V_0 - V_b &< \left\{\left(\frac{16}{9}\frac{\pi j}{\overset{+}{\mu}}\right)^{1/3}(x_b - x_0)\right\}^{3/2} \\ &> \left\{\left(\frac{16}{9}\frac{\pi j}{\overset{+}{\mu}}\right)^{1/3}(x_b - x_0) - \epsilon^{2/3}\right\}^{3/2} + \epsilon. \end{aligned} \tag{17}$$

For convenience of application this expression may be written in another form (in which the mobility $\overset{+}{\mu}$ is assumed proportional to the m.f.p., $\bar{\lambda}$, of the electrons, that is

$$\overset{+}{\mu} = g\bar{\lambda} \tag{17a}$$

g being a constant)

$$\begin{aligned} V_0 - V_b &< \left\{\left[\frac{16\pi}{9g}\right]^{1/3}(j\bar{\lambda}^2)^{1/3}\left(\frac{x_b - x_0}{\bar{\lambda}}\right)\right\}^{3/2} \\ &> \left\{\left[\frac{16\pi}{9g}\right]^{1/3}(j\bar{\lambda}^2)^{1/3}\left(\frac{x_b - x_0}{\bar{\lambda}}\right) - \epsilon^{2/3}\right\}^{3/2} + \epsilon. \end{aligned} \tag{18}$$

The variable quantities are here enclosed in parentheses ( ).

Fall of Potential in the Region of Rebound.—We shall assume that the positive ions in their last mean free path to the cathode are freely accelerated under the action of the electric field. Also that they rebound from the cathode with a fraction κ^2 of their incident energy, and so on with each return, finally transmitting their charge to the cathode simultaneously with the disappearance of their kinetic energy of rebound. To just what extent the presence of the gas should alter the results derived from these simpler assumptions, we have not attempted to solve.

The problem is, to find the effectual velocity of the positive ions in the region of rebound and then apply Poisson's equation as in the preceding part.

On its first journey inward each positive ion, having a charge e and mass m, reaches the cathode with a kinetic energy equal to V_be, the potential of the cathode for convenience being assumed zero.

On the first excursion outward the ion rebounds to x_1 at a distance $(x_k - x_1)$ from the cathode such that all of its kinetic energy is converted into potential energy, then it is driven again to the cathode. The potential V_1 of the first turning point is given therefore by the equation

$$V_1e = \kappa^2 V_be.$$

Likewise for the second turning point at x_2

$$\begin{aligned} V_2e &= \kappa^2 V_1e \\ &= \kappa^4 V_be, \end{aligned}$$

and so on for the others at x_3, x_4, $\cdots$.

The effectual velocity of the ion at any point x is obtained from the total length of time dt it is between the planes x and $x + dx$.

On its first journey inward (the potential at x being V) the velocity $v_{b,k}$ at x is given by the equation

$$\tfrac{1}{2}mv_{b,k}^2 = (V_b - V)e,$$

from which

$$v_{b,k} = +\sqrt{\frac{2e}{m}}(V_b - V)^{1/2}.$$

On its first excursion out and back it passes the point x twice with a velocity $v_{1,k}$ given by the similar equation

$$\begin{aligned} \tfrac{1}{2}mv_{1,k}^2 &= (V_1 - V)e \\ &= (\kappa^2 V_b - V)e, \end{aligned}$$

from which

$$v_{1,k} = \pm\sqrt{\frac{2e}{m}}(\kappa^2 V_b - V)^{1/2}.$$

Likewise we have

$$v_{2,k} = \pm\sqrt{\frac{2e}{m}}(\kappa^4 V_b - V)^{1/2}$$

$$\vdots \qquad\qquad \vdots$$

and finally

$$v_{p,k} = \pm\sqrt{\frac{2e}{m}}(\kappa^{2p} V_b - V)^{1/2},$$

in which we consider

$$x_p < x < x_{p+1},$$

so that on the pth excursion the ion passes between the planes x and $x + dx$ its last time.

The total length of time dt during which the ion is within the given space dx is then

$$dt = \frac{dx}{v_{b,k}} + \frac{2dx}{v_{1,k}} + \frac{2dx}{v_{2,k}} + \cdots + \frac{2dx}{v_{p,k}}.$$

Its effectual velocity at x is therefore

$$\frac{dx}{dt} = \frac{1}{\dfrac{1}{v_{b,k}} + \dfrac{2}{v_{1,k}} + \dfrac{2}{v_{2,k}} + \cdots + \dfrac{2}{v_{p,k}}}.$$

The positive current density at x is given by the equation

$$\overset{+}{j} = \overset{+}{\rho}\frac{dx}{dt},$$

from which

$$\overset{+}{\rho} = \frac{\overset{+}{j}}{\dfrac{dx}{dt}}$$

$$= \overset{+}{j}\left(\frac{1}{v_{b,k}} + \frac{2}{v_{1,k}} + \frac{2}{v_{2,k}} + \cdots + \frac{2}{v_{p,k}}\right).$$

For this vicinity the experimental results indicate that $\overset{-}{j}$ is an extremely small part of j, hence $\overset{-}{\rho}$ is negligible compared with ρ or $\overset{+}{\rho}$. We may then write the last equation

$$\rho = j\left(\frac{1}{v_{b,k}} + \frac{2}{v_{1,k}} + \cdots + \frac{2}{v_{p,k}}\right)$$

$$= \frac{j}{\sqrt{\dfrac{2e}{m}}}\{(V_b - V)^{-1/2} + 2(\kappa^2 V_b - V)^{-1/2} + \cdots + 2(\kappa^{2p} V_b - V)^{-1/2}\}.$$

Substituting this value of ρ in (5)

$$\frac{d^2V}{dx^2} = -\frac{4\pi j}{\sqrt{\frac{2e}{m}}}\{(V_b - V)^{-1/2} + 2(\kappa^2 V_b - V)^{-1/2} + \cdots + 2(\kappa^{2p} V_b - V)^{-1/2}\}.$$

Integrating

$$\left(\frac{dV}{dx}\right)^2 = \frac{16\pi j}{\sqrt{\frac{2e}{m}}}\{(V_b - V)^{1/2} + 2(\kappa^2 V_b - V)^{1/2} + \cdots + 2(\kappa^{2p} V_b - V)^{1/2}\} + \text{constant} \qquad (19)$$

which holds between the turning points p and $p + 1$. This equation cannot be integrated, but remembering that the distance between successive turning points is essentially infinitesimal one may assume the gradient between these points to be linear, its end values given by substituting in this equation.

Letting $V = V_b$ in (19) the integration constant is found equal to

$$\left(\frac{dV}{dx}\right)_b^2,$$

which quantity experiment shows to be negligible when compared with the average value of $(dV/dx)^2$ in the region under consideration.[1] Dropping then $(dV/dx)_b^2$ (19) gives for the first turning point, at x_1, since $V_1 = \kappa^2 V_b$,

$$\left(\frac{dV}{dx}\right)_1^2 = \frac{16\pi j V_b^{1/2}}{\sqrt{\frac{2e}{m}}}(1 - \kappa^2)^{1/2}.$$

For the second turning point, at x_2, $(dV/dx)_1^2$ being now the integration constant,

$$\left(\frac{dV}{dx}\right)_2^2 = \frac{16\pi j V_b^{1/2}}{\sqrt{\frac{2e}{m}}}\{(1 - \kappa^4)^{1/2} + 2\kappa(1 - \kappa^2)^{1/2} + (1 - \kappa^2)^{1/2}\}.$$

For the third, at x_3, $(dV/dx)_2^2$ being the integration constant,

$$\left(\frac{dV}{dx}\right)_3^2 = \frac{16\pi j V_b^{1/2}}{\sqrt{\frac{2e}{m}}}\{(1 - \kappa^6)^{1/2} + 2\kappa(1 - \kappa^4)^{1/2} + 2\kappa(1 - \kappa^2)^{1/2} + (1 - \kappa^4)^{1/2} + 2\kappa(1 - \kappa^2)^{1/2} + (1 - \kappa^2)^{1/2}\},$$

and so on.

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[1] For example, in case of the normal cathode fall with an aluminium cathode in hydrogen, the square of the gradient per mean free path of an electron at x_b is about 170, while the square of the average value between x_b and the cathode is about 150,000.

The mean gradients between consecutive turning points, being the average of these end values, may then be written, respectively,

$$\left(\frac{dV}{dx}\right)_{b,\,1} = -\sqrt{\frac{16\pi}{\sqrt{\frac{2e}{m}}}}\cdot j^{1/2}V_b^{1/4}c_{b,\,1},$$

$$\left(\frac{dV}{dx}\right)_{1,\,2} = -\sqrt{\frac{16\pi}{\sqrt{\frac{2e}{m}}}}\cdot j^{1/2}\cdot V_b^{1/4}\cdot c_{1,\,2},$$

and so forth—$c_{b,\,1}$, $c_{1,\,2}$, $\cdots$ being constants whose values depend simply on κ.

Obviously then

$$\int_b^k \frac{dV}{dx}dx = -\sqrt{\frac{16\pi}{\sqrt{\frac{2e}{m}}}}\cdot j^{1/2}V_b^{1/4}\{c_{b,\,1}(x_1 - x_b) + c_{1,\,2}(x_2 - x_1) + \cdots + c_{k-1,\,k}(x_k - x_{k-1})\}. \tag{20}$$

That is

$$V_b = \sqrt{\frac{16\pi}{\sqrt{\frac{2e}{m}}}}\cdot j^{1/2}V_b^{1/4}C(x_k - x_b), \tag{21}$$

in which C is a factor which depends not only on κ but increases with the total number of rebounds, hence should increase with V_b.

We have already assumed that $(x_k - x_b)$ is equal to the mean free path of the positive ions, hence proportional to the mean free path $\bar{\lambda}$ of the electrons. Then

$$(x_k - x_b) = a\bar{\lambda}.$$

Substituting in (21) and writing

$$P = aC,$$

we have for the fall of potential in the apparent cathode film

$$V_b = \left[\frac{16\pi}{\sqrt{\frac{2e}{m}}}\right]^{2/3}\cdot P^{4/3}(j\bar{\lambda}^2)^{2/3}, \tag{22}$$

in which P should be constant with constant values of V_b and κ, but increase with V_b. The first condition allows an interesting test of the theory to be made, namely, for the case under which the cathode fall is found to be constant over a wide range of gas pressures.

The Total Cathode Fall.—Adding (18) and (22) we have the cathode fall

$$V_0 < \left\{ \left[\frac{16\pi}{9g} \right]^{1/3} (j\bar{\lambda}^2)^{1/3} \left(\frac{x_b - x_0}{\bar{\lambda}} \right) \right\}^{3/2} + \left[\frac{16\pi}{\sqrt{\frac{2e}{m}}} \right]^{2/3} \cdot P^{4/3}(j\bar{\lambda}^2)^{2/3}$$

$$> \left\{ \left[\frac{16\pi}{9g} \right]^{1/3} (j\bar{\lambda}^2)^{1/3} \left(\frac{x_b - x_0}{\bar{\lambda}} \right) - \epsilon^{2/3} \right\}^{3/2} + \epsilon \qquad (23)$$

$$+ \left[\frac{16\pi}{\sqrt{\frac{2e}{m}}} \right]^{2/3} \cdot P^{4/3}(j\bar{\lambda}^2)^{2/3}.$$

These limits for V_0 suggest the simplest condition under which the cathode fall should remain constant with varying gas pressure. For this case the variable quantities in both expressions are

$$(j\bar{\lambda}^2) \quad \text{and} \quad \left(\frac{x_b - x_0}{\bar{\lambda}} \right),$$

the second being, within the errors of measurement, ***the number of mean free paths of the electrons between the cathode and the outer edge of the bright striation of the negative glow, where the gradient is a minimum.***

Providing the above limits of V_0 are not too greatly different,[1] V_0 should be constant if $(j\bar{\lambda}^2)$ and $[(x_b - x_0)/\bar{\lambda}]$ are constant.

The results of an experimental study of these magnitudes follow.

Experimental.

Apparatus.—A discharge tube (diam. 3 cm.) was provided with a circular disk cathode (area 3 sq. cm.) accurately adjustable in a direction perpendicular to its face by a screw actuated through a ground joint. A glass hood confined the current to the front face of the cathode. Two fine parallel probe wires (aluminium) lying in the equipotential surfaces, and sheathed to near their ends with very fine glass tubing, served to indicate (in connection with an electrometer) the point of minimum gradient in the negative glow.

It was soon found that, except at the lowest pressures and current densities, the point of minimum gradient, or more exactly the point at which the gradient suddenly began to increase from a zero value, was very closely marked by the luminosity as described on page 000. This being a much more convenient method of setting, it was largely used in the measurements.[2]

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[1] Calculations made from observations on an aluminium cathode in hydrogen show these limits of V_0 to differ at most by 12 per cent. (see Table VI.).

[2] Both methods of setting are subject to appreciable error at those low gas pressures where the minimum cathode fall begins to run above its so-called normal value.

Special care was taken to prevent, by sufficient insulation, any leakage current from the probe wires, as the corresponding fall of potential, if the wire for the leakage current is a cathode, has a very marked effect on the indicated value.[1]

The electric current was furnished by a battery of small storage cells, was measured by either a milli-ammeter or a more sensitive galvanometer, and regulated by a solution of cadmium iodide in amyl alcohol.

The cathode fall was measured by a Kelvin electrometer, being placed between the needle and one pair of quadrants, while a definite potential (10–20 volts) was placed between the quadrant pairs.

Normal Cathode Fall, Current Density and Distance to Negative Glow.—The gas chosen was hydrogen because of the relatively large distance it gives between the cathode and negative glow. The metals chosen were aluminium and steel which have respectively (among the common metals) the smallest and largest values of the cathode fall.

The hydrogen was generated from aluminium in a solution of potassium hydrate, then carefully dried in a chamber containing phosphorous pentoxide, and finally stored in a convenient bulb (freed of occluded gases), from which the supply was drawn as needed.

The cathode was always polished with infusorial earth and rubbed clean with new cloth just before mounting in the discharge tube. In addition its discharge surface was always cleaned by a heavy current (passed through the old gas just before evacuating and introducing the fresh). All measurements were made as soon as possible after this last cleaning was done. For each day's observations the cathode was always polished anew.

Tables I. and II. give a representative series of measurements for the two metals respectively. Each recorded pressure (first column) represents an entirely fresh gas filling.

With gas pressures ranging from one to five millimeters the normal cathode fall (second column) fluctuates irregularly about a constant value.

The normal current density (third column) was obtained either by increasing the current to the point where the cathode fall began to increase, or until the negative glow appeared of uniform intensity over the face of the cathode and did not curl away from it at any part—the latter method of setting being usually the more sensitive.

The distance from cathode to the position of minimum gradient was measured by the number of turns of the screw required to shift the cathode from contact with the fixed probe wire to where the wire was at the point of minimum gradient, located as already described.

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[1] In order to eliminate errors arising from leakage all lines to the electrometer including the battery used to charge the quadrants, and the electrometer itself had to be placed on sealing wax insulators—no "ground" to the electrometer being used.

Table I.

Aluminium Cathode in Hydrogen. Area of Cathode: 3.0 sq. cm.

Gas Pressure (Mm.).	Normal Fall (Volts).	Normal Current Density (j_n)	Distance to Neg. Glow ($x_k - x_0$).	Mean Free Path ($\bar{\lambda}$)	($j_n\bar{\lambda}^2$)	$\left(\frac{x_k - x_0}{\bar{\lambda}}\right)$
1.12	205	.10 m.a.	9.6 mm.	.64 mm.	.041	15
1.65	196	.19	6.8	.44	.037	15.5
2.27	194	.42	4.6	.315	.042	14.6
2.28	196	.43	4.5	.315	.043	14.3
2.41	206	.43	4.7	.30	.039	15.7
3.13	195	.67	3.6	.235	.037	15.3
3.58	194	.90	——	.20	.036	——
4.18	194	1.40	2.7	.17	.040	15.8
5.36	197	——	2.15	.135	——	15.9
Mean	197		Mean		.039	15.3
Max. dev.	4.5%		Max. dev.		10%	6.5%
Mean dev.	3%		Mean dev.		5%	3%

The mean free path of the electrons (column 5) which is inversely proportional to the gas pressure was obtained by multiplying the m.f.p. of the molecule by $4\sqrt{2}$.
ments of this magnitude.

Columns six and seven give respectively the calculated values of the quantities ($j\bar{\lambda}^2$) and $[(x_k - x_0)/\bar{\lambda}]$ which practically $= [(x_b - x_0)/\bar{\lambda}]$. The results show that, with constant cathode fall, gas pressures ranging from one to four times, and the normal current densities ranging from one

Table II.

Steel Cathode in Hydrogen. Area of Cathode: 3.0 sq. cm.

Gas Pressure (Mm.).	Normal Fall (Volts).	Normal Current Density (j_n).	Distance to Neg. Glow ($x_k - x_0$)	Mean Free Path ($\bar{\lambda}$)	($j_n\bar{\lambda}^2$)	$\left(\frac{x_k - x_0}{\bar{\lambda}}\right)$
1.30	310	.087 m.a.	11.7	.55	.0265	20.1
1.48	306	.10	10.2	.49	.024	20.8
1.73	305	.167	8.4	.42	.0295	20.0
1.95	313	.207	7.6	.37	.0285	20.5
2.11	306	.25	7.1	.34	.029	20.9
2.43	305	.300	5.7	.30	.027	19.0
2.72	305	.367	5.5	.265	.025	20.8
2.93	302	.467	5.1	.245	.028	20.8
3.31	298	.567	4.6	.215	.026	21.4
3.72	298	.767	4.1	.195	.029	21.0
4.00	302	.85	3.7	.18	.0275	20.6
4.77	289	1.20	2.9	.15	.027	19.3
5.00	304	1.33	3.0	.145	.028	20.8
Mean	303.5			Mean	.0273	20.5
Max. dev.	5%			Max. dev.	12%	7%
Mean dev.	2%			Mean dev.	5%	2½%

to sixteen, both of these magnitudes fluctuate irregularly about constant values—the deviation falling on the average well within the errors of observation.

Thus we find, as suggested by the foregoing theoretical deductions, that the *normal current density is inversely proportional to* $\bar{\lambda}^2$, *that is, proportional to the square of the gas pressure*[1]—nearly one and a half times as large with aluminium as it is with steel. Further, *the normal cathode fall extends from the cathode, at all gas pressures, the same number of mean free paths* of the electron. With a steel cathode this number is one and a third times that with an aluminium cathode, its fall being one and a half times as large.

These experimental results being favorable to the theory a more thorough investigation of its appplicability was desirable.

The Potential Curve in the Gas.—Preliminary measurements of the potential difference between the cathode and various distances $(x_k - x)$ in the gas (out to the negative glow), at various pressures and current densities, indicated that for the same values of $(j\bar{\lambda}^2)$ and $[(x_k - x)/\bar{\lambda}]$ the potential at x was always the same. That is, the potentials in the gas plotted against the number of mean free paths from the cathode, fell, for constant values of $(j\bar{\lambda}^2)$, on the same curve.

A systematic investigation of this was carried out with an aluminium cathode in hydrogen. The results are incorporated in Tables III., IV. and V. Each series of observations were made with fresh gas and a current-cleaned cathode. A series consisted in measuring the difference of potential between the cathode and a single probe wire (al., diam. .24 mm.) when the latter was placed at two, three, four, etc., mean free paths (measured to the center of the probe wire) from the cathode—the current density during that time being maintained at "normal," "twice-normal," or "four-normal" value. A disturbing source of error arises from the change in the gas, with duration of current, causing an increase in the potential difference. We are inclined to attribute this change to the presence of metal vapor from the cathode, as its effect is appreciably smaller with aluminium than with steel, and it is well known that the former gives off distinctly less material by the cathode spray than the other metals.

To avoid this error the observations were hurried through as rapidly as possible by three observers—one regulating the current, the second observing the electrometer deflection (to one side only), and the third setting the probe wire.

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[1] H. A. Wilson (Phil. Mag., Vol. VI, 4, p. 608) from a study of the current density with wire cathodes in air, concluded that at a determinate distance from the cathode surface the current density is proportional to the gas pressure.

TOTAL RADIATION FROM METALS.

By Vernon A. Suydam.

FROM a consideration of the experimental results thus far obtained the statement is justified that with many substances total radiation may be expressed with fair accuracy by a simple relation of the form

$$E = c'T^n. \tag{1}$$

In the case of some metals and alloys, however, this equation does not express the radiation accurately owing to irregularities in emission. In those cases where an equation of this form does hold n is not equal to 4, as Stefan supposed, except perhaps in exceptional cases. The character of the surface of the body and its internal structure are factors which affect radiation, and, as these vary with the temperature, it is to be expected that the emission cannot always be expressed so simply. From an application of Kirchhoff's law, which may be written

$$\frac{f(T)}{cT^4} = a(T), \tag{2}$$

coupled with the fact that $a(T)$ is a function of the temperature in most cases, it is easily seen that $f(T)$ is not equal to $c'T^4$. $f(T)$ may be of the form $c'T^n$, but n cannot be equal to 4 unless $a(T)$ is constant. The work of E. Hagen and H. Rubens shows $a(T)$ in the case of metals to be a function of the temperature for infra-red radiation, as it is made to depend upon the electrical resistance.[1] The coefficient of electrical resistance for metals is positive when the metal is in the solid state, and hence $a(T)$ increases with T, approaching unity as a limit. Hence metals approach black-body radiation with increase in temperature. The present investigation shows that glass, brass and lamp-black are better absorbers at high than at low temperatures. In the case of all the metals tested n was found to be greater than 4. This result agrees with the observations of F. Paschen and also E. Aschkinass.[2]

Method of Observation.

The metal to be tested was in the form of a wire which was stretched coaxially in a cylindrical enclosure, a light spring being used to keep it

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[1] Phil. Mag., 7, p. 157, 1904. Preuss, Akad. Wiss. Berlin Sitz. Ber., 23, p. 467, 1910.

[2] Drude Ann., 17, p. 960, 1905.

taut when heated. Fine platinum potential-wires were fused to the test-wire at points well removed from its points of entrance to the enclosure. In the case of silver the potential wires were silver soldered. The watt-input was calculated from the fall in potential between the points p_1p_2, Fig. 1 (measured with a low-resistance Leeds and Northrup potentiometer), and the current flowing. The current was calculated from the fall in potential over a known standard resistance, R, placed in series with the test-wire. The arrangement of the apparatus is indicated in Fig. 1.

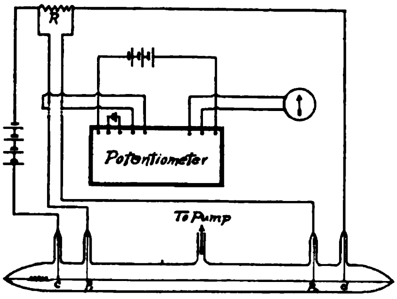

Fig. 1.

The temperature of the wire, for any given steady current, was determined from its resistance, which was calculated from the known current and fall in potential between the points p_1p_2. In order that the resistance of the wire might serve as a measure of its temperature it was necessary to obtain data for a temperature-resistance curve, from which the temperature corresponding to any given resistance, could be determined. The arrangement of the apparatus for obtaining such data is indicated in Fig. 2.

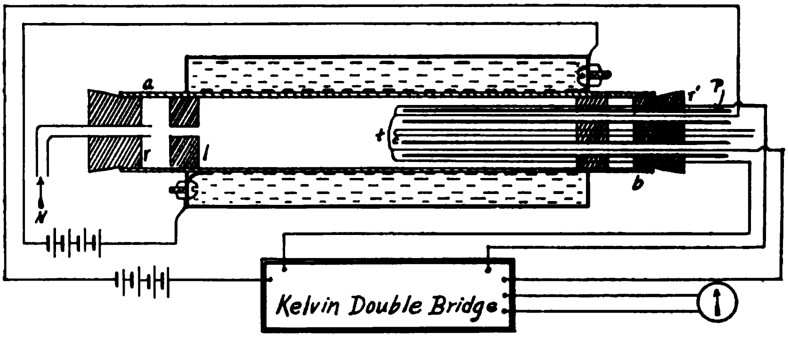

Fig. 2.

A long quartz tube, *ab*, wound with nichrome ribbon and packed in sand served as a heating furnace. The nichrome was protected from oxidation by being covered with a layer of alundum cement. With this arrangement the furnace could be heated to 1500° K. repeatedly. The ends of the quartz tube were sealed with rubber corks, *rr'*. To protect the rubber corks from the heat of the furnace lavite plugs, *l*, were inserted at a short distance from the corks. This gave sufficient protection for the temperature attained. Through the cork *r'* and the corresponding lavite plug were passed two porcelain tubes, *P*, and a Pt *vs.* Pt + 10 per cent. Rh thermocouple. This thermocouple was calibrated by comparing it with a standard thermocouple which had been calibrated at the Bureau of Standards. The wire, *t*, whose resistance was to be measured was placed in the center of the furnace with the hot junction, *c*, of the thermocouple close against it. The current terminals entered the furnace through the porcelain tubes, the potential terminals just outside a Leeds and Northrup Kelvin-double-bridge being used to measure the resistance. The wire was protected from oxidation by passing nitrogen through the furnace. The nitrogen was obtained after the method of G. A. Hulett.[1] This method consists in heating copper and copper oxide held in a hard-glass tube, and passing air and hydrogen through the tube. The hydrogen combines with the oxygen of the air and the emergent gas is pure nitrogen.

The metals tested were silver, platinum, nickel and iron, and the alloy nichrome. When platinum was tested the enclosure was made of brass blackened within with lamp-black. For all the other samples a glass enclosure was used. In all cases the surface of the test-wire was carefully cleaned and polished. Before taking a set of observations the wire was heated, by sending a strong current through it, in order to drive off accluded gases.

When the test-wire was platinum the temperature of the enclosure was first held at 90° K., by immersing it in liquid air, then at 273° K., by packing it in melting ice, and then at 373° K., by immersing it in boiling water. In other cases only the temperatures 273° K. and 373° K. were used as fixed temperatures. It was found that the temperature of the enclosure had an influence upon the watt-input. In every case the energy-temperature curve obtained by holding the enclosure at a low temperature was steeper than when it was held at a higher temperature, indicating that the reflecting power of the enclosure increased with decrease in temperature, or $a(T)$ increased with increase in temperature. A. Schleiermacher[2] in his report on radiation from platinum (his method of experimentation was the same as the one here used) observes that the

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[1] Jour. of Am. Chem. Soc., 27, p. 1415.

[2] Wied. Ann., 26, p. 287, 1885.

curves meet at a temperature somewhat above that of the highest temperature of the enclosure and states that they coincide above this temperature. The author found in his work that the curves cross but do not coincide at any temperature above the crossing point although they do not separate widely. Data are given here for only two cases, platinum and silver, where the temperature of the enclosure was other than 273° K., as it was found that the influence of the enclosure was negligible for temperatures of the test-wire large in comparison with that of the enclosure.

DISCUSSION.

The watt-input, which is measured, is the difference between the true emission from the metal when at a given temperature and the energy which it receives from the enclosure. This latter is made up of two parts: energy emitted by the enclosure and reflected from it. This action may be represented by the following functional equation:

$$f(T) = \omega(T) + a(T)\{r(T, T_e) + e(T_e)\}, \tag{3}$$

where $f(T)$ is the total radiation from the metal, $\omega(T)$ the watt-input, $a(T)$ the absorption coefficient, $r(T, T_e)$ the reflected energy, which depends upon the temperature, T, of the test-wire and the temperature T_e, of the enclosure, $e(T_e)$ the total radiation from the enclosure, constant for any given set of observations.

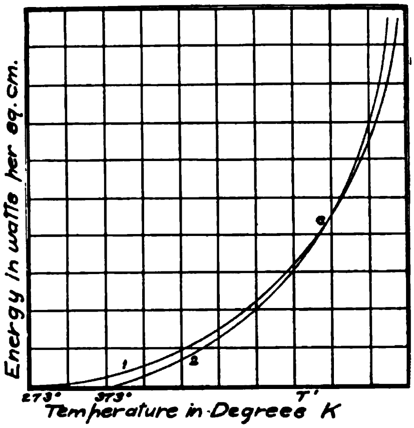

Fig. 3.

Referring to the accompanying diagram, Fig. 3, which is a representation of the curves obtained in this investigation, it is seen that at the point e, where the curves cross at temperature T'

$$\omega_1(T') = \omega_2(T'), \tag{4}$$

where the subscripts refer to the curves obtained when the enclosure was at 273° K. and 373° K. respectively. From equations (3) and (4) we obtain

$$r(T', T_{e_1}) - r(T', T_{e_2}) = e(T_{e_2}) - e(T_{e_1}). \tag{5}$$

The right-hand member of this equation is constant and depends only upon the substance and temperature of the enclosure. Since

$$e(T_{e_2}) > e(T_{e_1})$$

it follows that

$$r(T', T_{e_1}) > r(T', T_{e_2}).$$

That is, the quantity of energy reflected per second per unit area from the enclosure is greater when it is held at 273° K. than when held at 373° K. Thus in the case of all the enclosures used $a(T)$ increased with increase in temperature over the temperature range used in this investigation.

If there were no energy reflected from the enclosure the slope of the energy-temperature curve would be greater at every point with the temperature of the enclosure at 273° K. than at 373° K., because less energy would be sent to the test-wire from the enclosure. Since the reverse is the case, it follows that the enclosure is a better reflector at a low than at a high temperature, and hence that the reflected energy

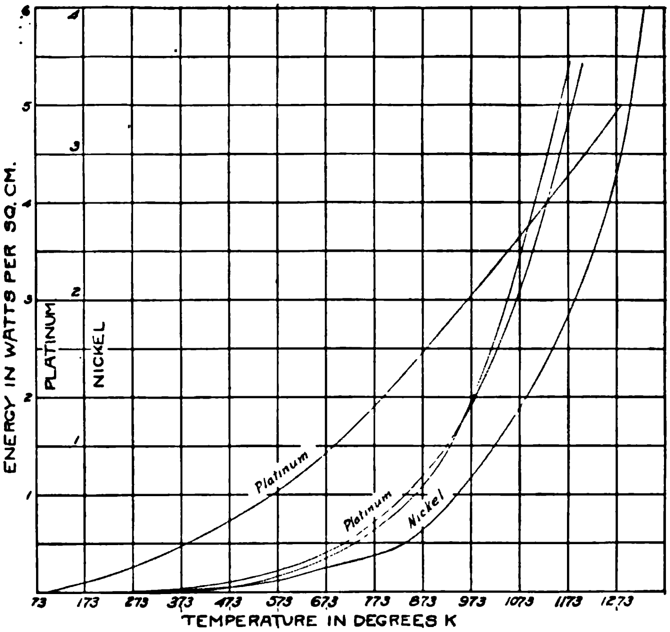

Fig. 4.

Energy-Temperature Curves.

plays a larger part in maintaining the temperature of the test-wire than does the emitted energy. This accounts for the crossing of the curves. That the curves do not separate more widely above the point of crossing seems to indicate a falling off of the percentage of reflected energy for higher temperatures of the test-wire. This may be accounted for from the fact that the energy emitted from the test-wire contains an ever increasing amount in short waves, and as the short waves are more readily absorbed and transmitted there will be a decrease in the percentage of reflected energy.

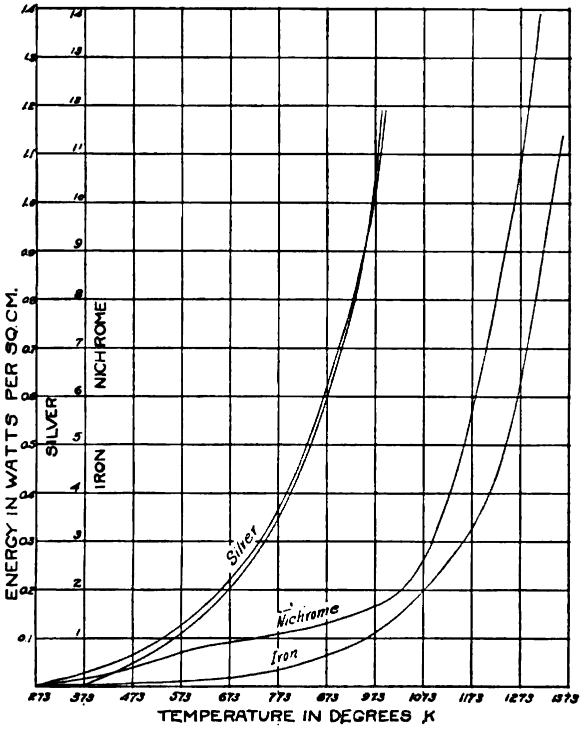

Fig. 5.

Energy-Temperature Curves.

Fig. 4 shows the energy-temperature curves obtained by holding the temperature of the enclosure at 90° K., 273° K. and 373° K. The test-wire was platinum and the enclosure was brass blackened within with lamp-black. It will be noticed that the slope of the curve in each case is greater when the temperature of the enclosure was maintained at a high temperature than when at a lower temperature. It requires less energy to maintain the temperature of the test-wire at, say, 1,133° K., with the enclosure at 90° K. than with the enclosure at 373° K. In the former case the energy required was 4.02 watts per sq. cm. and in the latter 4.51 watts per sq. cm.

From equations (2) and (3) we obtain

$$\omega(T) = f(T)\left\{1 - \frac{r(T, T_e) + e(T_e)}{cT^4}\right\}. \tag{7}$$

This equation shows that when $T = Te$

$$cT^4 = r(T, T_e) + e(T_e),$$

since $\omega(T) = 0$ and $f(T) \neq 0$. This is a statement for black-body radiation in an enclosure in thermodynamic equilibrium. In the development of this equation no account has been taken of extraneous radiation that might enter the enclosure from without, and it has been assumed that the enclosure reflects and emits energy as though equal in area to that of the test-wire.

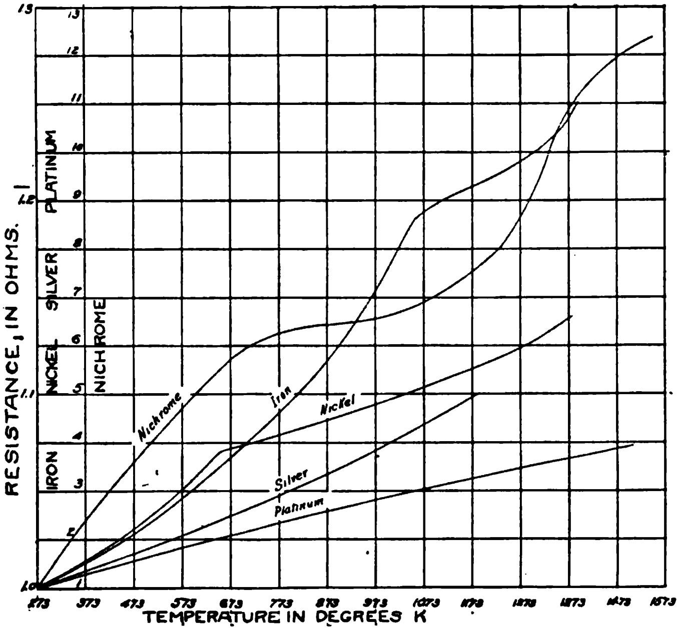

Fig. 6.

Resistance-Temperature Curves; reduced to one ohm at 273° K.

In order to calculate approximately the relative magnitudes of $\omega(T)$ and $f(T)$ in equation (7) it is necessary to evaluate the terms in brackets. L. Graetz[1] found that glass conforms very nearly to black-body radiation for temperatures lying between 273° K. and 456° K., and gives as the average value for c

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[1] Wied. Ann., 11, p. 913, 1880.

$$4.52 \times 10^{-12} \frac{\text{watt}}{\text{cm.}^2 \text{ sec. temp.}^4}.$$

For a black-body c is

$$5.65 \times 10^{-12} \frac{\text{watt}}{\text{cm.}^2 \text{ sec. temp.}^4}.$$

Using these values we obtain, by substituting in the last term of the right-hand member of equation (7),

$$\frac{e(T_e)}{cT^4} = \frac{4.52 \times 10^{-12} \times 273^4}{5.65 \times 10^{-12} \times 950^4} = 0.00545,$$

the temperature 950° K. being taken from Table II. Applying Kirchhoff's law to this case we find

$$\frac{e(T)}{cT^4} = \frac{4.52 \times 10^{-12} T^4}{5.65 \times 10^{-12} T^4} = 0.80 = a(T).$$

This gives 20 per cent. for the reflecting power of glass in the temperature interval here used. As a first approximation we may take $\omega(T)$ as equal to $f(T)$. Referring to Table II., the watt-input for silver at $T = 950°$ K. is found to be 0.4903 watt per sq. cm. 20 per cent. of this is 0.098, which is the amount returned to the wire, $r(T, Te)$. Substituting this value in the term next to the last in the right-hand member of equation (7) we find

Table I.

Platinum.

$T_e = 90°$ K.		$T_e = 273°$ K.		$T_e = 373°$ K.	
Temp. in Deg. K.	**Emission in Watts per Sq. Cm.**	**Temp. in Deg. K.**	**Emission in Watts per Sq. Cm.**	**Temp. in Deg. K.**	**Emission in Watts per Sq. Cm.**
115	0.0291	541	0.1540	534	0.1271
126	0.0472	596	0.2323	572	0.1721
144	0.0734	647	0.3293	642	0.2586
201	0.1682	698	0.4562	699	0.3954
283	0.2650	772	0.7104	725	0.4886
351	0.4500	834	0.9776	802	0.7233
487	0.7557	879	1.2477	870	1.0522
567	1.0000	914	1.4726	917	1.3845
632	1.2527	981	2.0338	944	1.6741
723	1.6490	991	2.1597	979	2.0582
786	1.9905	1,018	2.4129	1,007	2.3975
863	2.4250	1,046	2.7412	1,044	2.8930
914	2.7746	1,091	3.3427	1,048	2.9482
1,134	4.0079	1,118	3.7820	1,100	3.7880
1,166	4.2512	1,148	4.2532	1,135	4.4696

$$\frac{r(T, T_e)}{cT^4} = \frac{0.098}{5.65 \times 10^{-12} \times 950^4} = 0.0218.$$

The substitution of these values in equation (7) gives a first approximate value for $f(T)$. Thus

$$\omega(T) = 0.973 f(T).$$

Other errors for which no corrections have been made would change this relation slightly. There is a small loss of energy, due to conduction along the potential wires and in the residual gas and volitalization of the metal, which tends to make $\omega(T)$ too large.

To a close approximation, therefore, $\omega(T)$ may be taken as equal to $f(T)$ for values of T large in comparison with Te. Thus for high temperatures the watt-input, $\omega(T)$, is a function of the same form and of the same order of magnitude as $f(T)$. A. Schleiermacher concludes from the fact that the curves nearly coincide for large values of T that the reflection and radiation from the walls of the enclosure are relatively unimportant.

RESULTS.

Silver.—The diameter of the wire used was 0.0128 cm., and the length between potential points was 44 cm. Silver was found to conform to the fourth-power law more nearly than any of the other metals tested. Its emission may be represented very accurately by the equation

$$E = c'T^{4.1},$$

where c has the mean value of 2.91×10^{-13} when the temperature of the enclosure was 373° K., and 3.07×10^{-13} when it was 273° K. The enclosure was glass. Only one sample of sliver was tested, but many sets of observations on several wires cut from the same coil gave very consistent results.

TABLE II.

Silver.			Silver.		
$T_e = 273°$ K. Average Pressure = 0.0002 Mm.			$T_e = 273°$ K. Average Pressure = 0.0002 Mm.		
Temp. in Deg. K.	Emission in Watts per Sq. Cm.	c'.	Temp. in Deg. K.	Emission in Watts per Sq. Cm.	c'.
610	0.0859	3.26×10^{-13}	625	0.0875	3.01×10^{-13}
686	0.1313	3.09×10^{-13}	697	0.1306	2.88×10^{-13}
738	0.1735	3.02×10^{-13}	749	0.1741	2.99×10^{-13}
805	0.2435	2.97×10^{-13}	805	0.2595	3.16×10^{-13}
885	0.3693	3.05×10^{-13}	869	0.3279	2.92×10^{-13}
950	0.4903	3.03×10^{-13}	901	0.3927	3.01×10^{-13}
			945	0.4739	3.00×10^{-13}
			981	0.5691	3.08×10^{-13}

TABLE III.

Platinum.			Platinum.		
$T_e = 273°$ K. Av. Pressure = 0.0014 Mm.			$T_e = 373°$ K. Av. Pressure = 0.003 Mm.		
Temp. in Degrees K.	Emission in Watts per Sq. Cm.	c'.	Temp. in Degrees K.	Emission in Watts per Sq. Cm.	c'.
647	0.3293	2.90×10^{-15}	642	0.2586	2.43×10^{-15}
698	0.4562	2.75×10^{-15}	699	0.3954	2.37×10^{-15}
772	0.7104	2.59×10^{-15}	725	0.4886	2.44×10^{-15}
834	0.9776	2.42×10^{-15}	802	0.7233	2.18×10^{-15}
879	1.2477	2.38×10^{-15}	870	1.0522	2.11×10^{-15}
914	1.4726	2.31×10^{-15}	917	1.3845	2.14×10^{-15}
981	2.0338	2.24×10^{-15}	944	1.6741	2.23×10^{-15}
991	2.1597	2.26×10^{-15}	979	2.0582	2.29×10^{-15}
1,018	2.4129	2.21×10^{-15}	1,007	2.3975	2.31×10^{-15}
1,046	2.7412	2.19×10^{-15}	1,014	2.8930	2.33×10^{-15}
1,091	3.3427	2.16×10^{-15}	1,048	2.9482	2.33×10^{-15}
1,118	3.7820	2.16×10^{-15}	1,100	3.7880	2.35×10^{-15}
1,148	4.2532	2.13×10^{-15}	1,135	4.4696	2.37×10^{-15}

TABLE IV.

Nichrome.			Nickel.		
$T_e = 273°$ K. Av. Pressure = 0.0002 Mm.			$T_e = 273°$ K. Av. Pressure = 0.0002 Mm.		
Temp. in Degrees K.	Emission in Watts per Sq. Cm.	n.	Temp. in Degrees K.	Emission in Watts per Sq. Cm.	n.
325	0.0417	4.13	463	0.0258	4.65
392	0.1168	4.17	518	0.0462	4.66
483	0.3259	4.19	603	0.1000	4.67
540	0.5973	4.18	643	0.1343	4.70
673	0.9080	4.14	661	0.1526	4.67
823	1.2349	4.06	711	0.1935	4.68
1,013	1.8913	4.00	773	0.2408	4.62
1,073	2.6900	4.02	803	0.2808	4.62
1,113	3.6500	4.05	883	0.4498	4.63
1,163	5.3282	4.07	923	0.5852	4.63
1,178	5.9170	4.07	951	0.7012	4.64
1,228	8.2590	4.10	1,028	1.0484	4.64
1,258	9.8000	4.11	1,071	1.2553	4.64
1,283	11.5910	4.12	1,123	1.5499	4.64
1,308	13.3820	4.13	1,181	1.9324	4.64
			1,283	2.9572	4.65

Platinum.—Two specimens of platinum were tested with good agreement in results. Many sets of observations were taken on each specimen. The temperature-resistance curve for the specimen contained in this report was plotted from the equation

$$\rho_t = \rho_0(1 + \alpha t + \beta t^2),$$

where $\rho_0 = 1$ ohm, $\alpha = 0.0028$, $\beta = -0.00000033$. The enclosure was brass coated within with lamp-black. The diameter of the wire was 0.0159 cm. and its length between potential points was 40.3 cm. The emission was found to conform to the equation

$$E = c'T^5,$$

TABLE V.

Iron.		
$T_e = 273°$ K. Av. Pressure = 0.0002 Mm.		
Temp. in Degrees K.	**Emission in Watts per Sq. Cm.**	**c'.**
696	0.2230	3.54×10^{-17}
753	0.3103	3.35×10^{-17}
805	0.4362	3.25×10^{-17}
853	0.5661	3.06×10^{-17}
915	0.7952	2.89×10^{-17}
975	1.1604	2.99×10^{-17}
1,083	2.1810	3.13×10^{-17}
1,133	2.7135	3.04×10^{-17}
1,180	3.3628	3.00×10^{-17}
1,192	3.5813	3.02×10^{-17}
1,233	4.7000	3.29×10^{-17}
1,240	4.9420	3.35×10^{-17}
1,303	7.8800	3.99×10^{-17}

TABLE VI.

Platinum.		Silver.		Nichrome.	
Temp. in Degrees K.	**Resistance in Ohms.**	**Temp. in Degrees K.**	**Resistance in Ohms.**	**Temp. in Degrees K.**	**Resistance in Ohms.**
273	1.000	273	1.000	273	1.000
373	1.280	323	1.145	317	1.020
473	1.553	373	1.350	339	1.033
573	1.820	423	1.510	398	1.045
673	2.079	477	1.720	448	1.058
773	2.332	523	1.889	503	1.073
873	2.579	574	2.070	556	1.088
973	2.816	623	2.275	606	1.103
1,073	3.049	683	2.520	668	1.118
1,173	3.275	723	2.685	735	1.128
1,273	3.494	792	3.000	867	1.133
1,373	3.706	823	3.105	945	1.138
1,473	3.911	854	3.240	1,018	1.143
1,573	4.109	913	3.545	1,058	1.149
1,673	4.300	953	3.730	1,103	1.154
		1,073	4.355	1,188	1.169
				1,238	1.179
				1,285	1.199
				1,320	1.219
				1,352	1.239
				1,375	1.249
				1,503	1.279

where c has the mean value of 2.36×10^{-15} when the enclosure was at 273° K. and 2.29×10^{-15} when it was at 373° K.

Nickel.—The diameter of the wire for which data are here given was 0.0455 cm. and its length between potential points was 29.8 cm. The energy-temperature cuvre suffers a slight variation in the neighborhood of the temperature at which recalescence occurs. In this neighborhood the emission increases less rapidly with rising temperature than either above or below. The variation in emitting power occurs at about the same temperature as that at which there is a pronounced variation in the coefficient of electrical resistance but does not persist over as great a range of temperature. The equation $E = c'T^n$ does not hold for nickel as well as for platinum. By holding c' constant — $c' = 1.04 \times 10^{-14}$— the variations in n are exhibited. The data for nickel are given in Table IV. n has the average value 4.648. Since nickel showed a variation from the Stefan equation at about the temperature 650° K. several different samples were tested with many sets of observations. The results were uniformly the same. With any given sample the curves could be reproduced with great accuracy.

Table VII.

Iron.		Nickel.	
Temperature in Degrees K.	Resistance in Ohms.	Temperature in Degrees K.	Resistance in Ohms.
273	1.000	273	1.000
308	1.202	348	1.400
376	1.568	448	1.970
411	1.777	512	2.649
481	2.196	555	2.868
511	2.406	591	3.200
588	2.945	625	3.542
611	3.138	651	3.808
669	3.644	704	3.945
694	3.870	730	4.028
763	4.541	766	4.138
813	5.037	790	4.243
851	5.491	824	4.359
904	6.020	900	4.621
948	6.799	980	4.801
983	7.322	1,009	4.966
1,028	8.211	1,070	5.132
1,093	8.891	1,113	5.298
1,177	9.361	1,153	5.463
1,231	9.623	1,193	5.610
1,271	9.806	1,273	5.920
1,290	9.937		
1,328	10.198		
1,363	10.632		

Iron.—The diameter of the wire for which data are here given was 0.0476 cm., and its length between potential points was 29.9 cm. There is a pronounced change in the coefficient of electrical resistance in iron at about the temperature 1050° K. However, contrary to expectation, no variation in its emitting power was detected at this temperature. The energy-temperature curve was regular and conformed to Stefan's equation very well. This point was examined carefully. Different samples of iron were tested with great care but none of them showed any variation in emitting power at this temperature. c' has the average value 3.23×10^{-17} when n is taken equal to 5.55.

Nichrome.—The diameter of the wire was 0.046 cm. and its length between potential points was 24.6 cm. The temperature-resistance curve for nichrome suffers a pronounced change in the temperature interval 743° K. to 1043° K. In this same temperature range the energy-temperature curve varies. The emission from nichrome does not conform well to the equation $E = c'T^n$. The variations from this equation are shown by holding c' constant—$c' = 1.76 \times 10^{-12}$—and calculating n, Table IV. The samples of nichrome which were tested were all cut from the same coil. Many sets of observations were taken with uniformly consistent results.

This investigation was undertaken at the suggestion of Professor Augustus Trowbridge. The author takes this occasion to express his appreciation for the interest taken in this work by Professor Trowbridge and for the many helpful suggestions which were offered by him during its progress.

Palmer Physical Laboratory,
Princeton University,
June, 1914.

THE MAXWELL DISTRIBUTION LAW IN NEWTONIAN AND NON-NEWTONIAN MECHANICS.

BY GILBERT N. LEWIS AND ELLIOT Q. ADAMS.

SINCE Maxwell first obtained the law for the distribution of the molecules of a perfect gas with respect to velocity, numerous derivations of this law have been offered, and much discussion has ensued as to the logical rigor of these derivations. The method which has received the most attention in recent years is based upon the theorem of Liouville, and it is this method which has been used by Jüttner[1] and more recently by Tolman[2] in discussing what modifications of the Maxwell equation are necessitated by the assumption of the mechanics of relativity.

Without discussing the difficult questions which may arise, concerning the complete mathematical validity of these derivations, we wish, on account of the great theoretical importance of this subject, to offer an entirely independent method of deriving the distribution law,—in the non-Newtonian as well as in the Newtonian case,—a method which, as far as we can now see, is as rigorous as the fundamental principles of mechanics and geometry on which it is based.

In order to be as free as possible from non-essentials we shall consider the simplest possible case, namely, an ideal monatomic gas, in other words a system of like particles which are capable of acquiring only kinetic energy, situated in no directing field such as that of gravitation, and subject to the restriction that no portion of the gas, macroscopically considered, be in motion with respect to the common center of mass of the system. Our fundamental assumption will therefore be one of complete symmetry with respect both to position and to direction.

THE NEWTONIAN CASE.

Let us consider a system of gas molecules in temperature equilibrium. At a given instant, the vector momentum of each particle being determined, we may plot from a common center in three-dimensional space each of these vectors. The points which are the termini of these vectors

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[1] Ann. Phys., 4, 34, 856 (1911).

[2] Phil. Mag., 28, 583 (1914).

will therefore be used to represent the momenta of the several particles, both in magnitude and direction. Moreover, since the particles are of the same size, these points may also represent the individual velocities. Thus two points in Fig. 1, lying on the same radius vector from O, represent two particles moving in the same direction with different velocities; while two points equidistant from O represent two particles moving in different directions with the same scalar velocity.

Now since by assumption the particles can acquire no energy except kinetic, every collision between two particles[1] is elastic,[2] and the relative velocity of the two will change in direction but not in magnitude. Since the center of gravity of the two particles taken together remains fixed, a pair of points (A, B) must by collision be converted into two other points (C, D) such that the center of the line CD coincides with the center of the line AB. In other words, CD is another diameter of the sphere of which AB is a diameter.

If, in the figure, O represent the point of rest and P the center of any sphere, of which AB and CD represent any two diameters, the chance that a collision of a particle at A with one at B give a particle at C and one at D is equal to the chance that a collision of a particle at C with one at D produce particles at A and B, and this regardless of the nature of the forces during collision, for to an observer at P the diameters AB and CD differ only in direction. This is equivalent to the statement that the fraction of collisions (A, B) resulting in (C, D) and the fraction of collisions (C, D) resulting in (A, B) are equal.

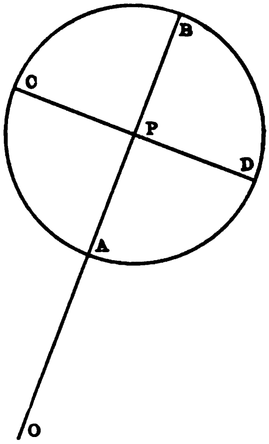

Fig. 1.

If the whole space of our figure be divided into equal infinitesimal regions the condition of equilibrium with respect to velocity distribution is that the number of particles leaving any region A in a given time is the same as the number entering. Owing to our conditions of symmetry this is equivalent to the more special condition that the number of

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[1] By the definition of an ideal gas we may exclude the case of simultaneous collisions of three or more particles, for by diminishing the concentration of the gas the number of such collisions falls off with the cube, at least, of the concentration while the number of simple collisions falls off only with the square.

[2] In order that the particles should possess no energy except kinetic, collision must be not only elastic but instantaneous, that is, the time during which the particles are subjected to mutual forces must be negligible in comparison with the interval between collisions. This is a condition approached by an actual monatomic gas as the concentration is indefinitely diminished.

particles in the region A which collide with particles in any other region B to give particles in regions C and D (where CD is another diameter of the sphere AB) is equal to the number of particles from C and D going into A and B. If this be true throughout the space the number of particles in each region will obviously remain constant.

We have shown that the chance that any pair of particles leaving the regions A and B enter the regions C and D is equal to the converse chance. The number of collisions of particles in A with particles in B to produce particles in C and D will be proportional to the product of the number in A by the number in B, and the number of collisions between particles in C and D to give particles in A and B is proportional to the product of their numbers. Moreover the proportionality factor will be the same in both cases owing to the symmetry about the point P which we have already pointed out. If n_A represent the number of particles in A, etc., our condition of thermal equilibrium is therefore

$$n_C n_D = n_A n_B. \tag{1}$$

Since the distribution of particles with respect to velocity depends only upon the scalar magnitude of the velocity, that is, upon the scalar distances OA, etc., n is a function of that scalar distance only, and we now have sufficient data for the complete determination of this functional relation.

Since equation (1) is true in general, it is true for the special case which we shall now, for convenience, assume, namely when AB is in the line of OP, and CD is perpendicular to it. In this case $OC = OD = \sqrt{r^2 + a^2}$ where $OP = r$ and $AP = a$. Also $OA = r - a$, $OB = r + a$, and, writing $f(OA)$ for n_A, equation (1) becomes

$$[f(\sqrt{r^2 + a^2})]^2 = f(r - a)f(r + a).$$

Taking logarithms

$$2 \ln f(\sqrt{r^2 + a^2}) = \ln f(r - a) + \ln f(r + a).$$

If now we write $\ln f(\sqrt{x}) = F(x)$

$$2F(r^2 + a^2) = F([r - a]^2) + F([r + a]^2).$$

If $(r - a)^2 = x$ and $(r + a)^2 = y$, $r^2 + a^2 = (x + y)/2$, and

$$2F\left(\frac{x + y}{2}\right) = F(x) + F(y).$$

Taking the partial derivative with respect to x, and to y

$$F'\left(\frac{x + y}{2}\right) = F'(x),$$

$$F'\left(\frac{x + y}{2}\right) = F'(y),$$

where F', as usual, represents the derivative of F with respect to its own argument.

Since we have already used the fact that x and y are completely independent, OA and OB being any two distances, F' is a constant and F a linear function, thus, choosing r^2 as the argument,

$$F(r^2) = A + Br^2,$$

or by our previous convention,

$$ln\, f(r) = A + Br^2,$$

$$f(r) = e^{A+Br^2} = ke^{Br^2},$$

where $k = e^A$.

Now $f(r)$ is the number of particles in a certain infinitesimal volume of our space, and r measures the numerical velocity. In order to give the number of particles between r and $r + dr$, or rather between the velocities v and $v + dv$, we must write

$$\frac{dn}{dv} = \alpha v^2 e^{Bv^2}, \tag{2}$$

where the relation of the new constants to the former depends upon the units of r and v. This is the customary form of the Maxwell equation.

The General Distribution Law.

In generalizing the proof which we have just given, to include the concepts of relativity and thus to obtain an equation valid for particles of any mass at any temperature, we must proceed with great care. Thus, in the preceding paragraphs, we have assumed, as is justified in the limiting Newtonian case, that there is no ambiguity in speaking of the number of particles leaving a certain momentum region in a given time; whereas in the kinematics of Einstein, time has no definite significance except with reference to an arbitrary zero of velocity. But, if care be taken to eliminate such ambiguities, the first postulate of relativity itself permits the use of just such principles of symmetry as we have already employed.

Since the epoch-making work of Minkowski the science of kinematics may be regarded as a pure four-dimensional geometry. If intervals of space and time are to be made real intervals of length in this geometry, the geometry proves to be the same as the Euclidean except for a single postulate, namely, the Euclidean postulate that in any plane a circle may be constructed by the rotation of any line about one of its extremities. The non-Euclidean geometry which results from a change in this postu-

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[1] "The Space-Time Manifold of Relativity. The Non-Euclidean Geometry of Mechanics and Electromagnetics," Proc. Amer. Acad., 48, 389 (1912).

late has been discussed in some detail by Wilson and Lewis,[1] whose nomenclature and methods we shall employ here.

According to the principle of relativity, the choice of a zero velocity and thus of a standard of time, is as purely arbitrary as the choice of special coördinates in ordinary geometry. But in a given problem such a choice is often prescribed by considerations of convenience, and this is the case in the problem we are now considering. We shall assume the system of gas molecules as a whole to be at rest, and the locus in four dimensions of the center of mass of the system to determine the standard axis of time. This standard of time determines standard space and standard volume. We may, however, when occasion arises, consider any one of the molecules at rest and thus fix what we may call the proper time (Eigenzeit), and the proper volume, corresponding.

In order to give a geometrical picture of the system under consideration we may in the first instance consider a system of molecules which are free to move not in a given volume but in a given plane area, like balls upon a billiard table. We thus reduce the geometry from four dimensions to three, and we have attempted in Fig. 2 to illustrate this simpler case. But in order to avoid a repetition of the proof we may generalize as we proceed, substituting spheres for circles, pseudo-spheres for pseudo-circles, hypercones for cones, etc.

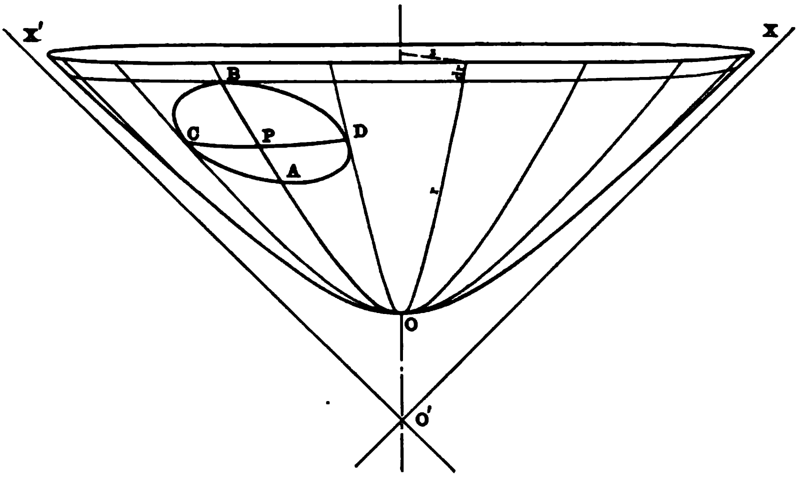

Fig. 2.

In the figure, $O'X$, $O'X'$ are elements of the singular cone (hypercone). They represent for example the locus of something moving with the velocity of light. A line within the cone (hypercone) represents the locus of any particle moving with a velocity less than that of light. If the particle is unaccelerated this locus is straight, and a vector along this line, of magnitude m_0—the mass of the particle at rest—is the "vector of extended momentum" of the particle. Its projections on a chosen time axis and upon the perpendicular plane (planoid) are respectively the ordinary mass and momentum of the particle.

If $O'O$ represent such a vector, then the vectors representing all possible motions of the same particle, or of other particles of the same m_0, terminate on the pseudo-sphere (hyper-pseudo-sphere) shown in the figure. For convenience we may choose such units that the m_0 of the particles and therefore the radius of the pseudo-sphere (hyper-pseudo-sphere) is unity. If now the vectors of extended momentum of all the gas molecules be drawn from O', the terminus of each will be a point upon the pseudo-sphere (hyper-pseudo-sphere) and our problem is the determination of the distribution of these points upon that surface (hyper-surface).

We shall show in an appendix to this article that this surface (hyper-surface) has all the properties of a Lobatschewskian plane (space) of unit space-constant, and the straight line of which is its intersection with any plane through O'. Our problem is therefore analogous to the one we have already treated, but the geometrical laws are those of Lobatschewskian space.

In the first place it is evident that if $O'O$ is the locus of one of the particles at rest, the distribution of the points representing vector-termini must be symmetrical about O; that is, if the whole surface (space) be divided as before into equal infinitesimal areas (volumes) the number in the region at a point A is a function of the distance OA alone.

If A and B be any two points, a collision between a particle at A and a particle at B will result in particles at some points C and D such that CD and AB are diameters of the same circle (sphere). This result follows at once from the law of the conservation of extended momentum,[1] or we may obtain it without the aid of this principle by considering an observer moving with a particle at P, the middle point of AB. To such an observer particles A and B are moving with equal and opposite velocities and their common center of mass is at rest. The center of mass will evidently remain at rest after collision and if the collision is elastic the scalar velocities with respect to that center will also remain unchanged. In other words, C and D must be such points that P is the center of CD and that $PC = PA$.

Now it is again evident from the symmetry about P that a collision between a pair of particles (A, B) has the same chance in resulting in a

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[1] Wilson and Lewis, loc. cit.

pair of particles (C, D) as a collision of the pair (C, D) has to produce the pair (A, B). Therefore the condition for permanency of distribution is that, from the standpoint of any one observer, the number of particles passing from (A, B) to (C, D) per second is equal to the number passing from (C, D) to (A, B). We shall naturally choose the common center P as the point of observation.

Now as far as the individual molecules are concerned the symmetry about P is perfect and we might be tempted to assume that once more the condition of stability could be written $n_C n_D = n_A n_B$. But we must remember that the particles A, B, C and D are not symmetrically placed with respect to the center of mass of the system, or, in other words, the enclosure containing the gas is not at rest with respect to P.

It was not necessary to point out in our previous proof that the frequency of collisions depends not merely upon the number of molecules of the kind considered but also upon the volume of the enclosure, for this volume was assumed to have definite significance, without further qualification. But in our present case the volume of the enclosure will appear different to observers moving with the different molecules. If, however, we consider not the number but the concentration by volume of particles in a region A, and if by concentration we mean the "proper" concentration as measured by an observer at A, then we may employ the principle of symmetry and write as the condition of equilibrium

$$C_C C_D = C_A C_B, \tag{3}$$

where C_A is the proper concentration at A, measured at A, C_B the proper concentration at B, measured at B, etc.

We shall once more choose the simple case where AB is an extension of OA and CD is perpendicular. Replacing C_A by $f(OA)$ we may write

$$f(OC)f(OD) = f(OA)f(OB)$$

and according to the proposition corresponding to the Pythagorean in Lobatschewskian geometry

$$\cosh(OC) = \cosh(OD) = \cosh(OP)\cosh(PC),$$

or writing, as before, $OP = r$, $PA = PC = a$, $OA = r - a$,

$$OB = r + a,\ OC = \cosh^{-1} (\cosh r \cosh a):$$

$$[f(\cosh^{-1} [\cosh r \cosh a])]^2 = f(r - a)f(r + a).$$

This functional equation may be uniquely solved as follows: Taking logarithms

$$2\, ln\, f(\cosh^{-1} [\cosh r \cosh a]) = ln\, f(r - a) + ln\, f(r + a).$$

Defining a new function,

$$F(x) = ln\, f(\cosh^{-1} x), \tag{4}$$

$$2F(\cosh r \cosh a) = F(\cosh [r - a]) + F(\cosh [r + a]),$$

or since $\cosh r \cosh a = \frac{1}{2}\cosh (r - a) + \frac{1}{2}\cosh (r + a)$,

$$2F(\tfrac{1}{2}\cosh[r - a] + \tfrac{1}{2}\cosh[r + a]) = F(\cosh[r - a]) + F(\cosh[r + a]).$$

Taking partial derivatives with respect to $\cosh (r - a)$ and $\cosh(r + a)$, respectively, which are independent since $(r - a)$ and $(r + a)$ may be varied independently at will,

$$F'(\tfrac{1}{2}\cosh [r - a] + \tfrac{1}{2}\cosh [r + a]) = F'(\cosh [r - a]),$$

$$F'(\tfrac{1}{2}\cosh [r - a] + \tfrac{1}{2}\cosh [r + a]) = \qquad F'(\cosh [r + a]),$$

or $F'(\cosh [r - a]) = F'(\cosh [r + a])$, hence F' is evidently a constant and F a linear function, or,

$$F(\cosh r) = A + B \cosh r,$$

whence by (4)

$$ln\, f(r) = A + B \cosh r$$

and

$$f(r) = ke^{B \cosh r} \tag{5}$$

where $k = e^A$.

Now $f(r)$ is the proper concentration at the distance r from O. If we take unit volume of the gas as measured by an observer at rest with respect to the system as a whole, that which is the proper unit volume at the distance r is less than unity measured in standard volume, in the ratio sech r. Hence the standard density is greater than the proper density at that point in the ratio $\cosh r$, for if r is the distance from O to any point such as A, then the angle $OO'A$ is equal to this arc r of the pseudo-circle, and the hyperbolic tangent of this angle ($\tanh r$) is the ordinary scalar velocity in the space perpendicular to OO' (the velocity of light taken as unity). Therefore $\cosh r = 1/\sqrt{1 - v^2}$ which is the familiar factor for the reduction of volumes at rest to volumes in motion.

The actual number of particles in any one of our equal infinitesimal regions is therefore not $f(r)$, but $\cosh r\, f(r)$. We shall therefore write for this number from equation (5)

$$\cosh r\, f(r) = k \cosh r\, e^{B \cosh r}.$$

Now this number is an infinitesimal region at distance r, multiplied by the number of such regions lying between r and $r + dr$, which is proportional to the area (volume) of the space thus cut out, gives the total number of particles lying between these limits. This area (volume) is equal to dr multiplied by the circumference (surface) of the Euclidean circle (sphere) of radius s, namely, $2\pi s\, dr$, $(4\pi s^2 dr)$. Now s in our relativity geometry is equal to $\sinh (OO'A) = \sinh r$, and (abandoning now the case of particles in a plane)

$$\frac{dN}{dr} = 4\pi k \sinh^2 r \cosh r\, e^{B \cosh r}. \tag{6}$$

This is the fundamental law for the distribution of gas particles with respect not to velocity but to the angle in our relativity space, of which the hyperbolic tangent is the velocity. We may put it in another form, writing $\cosh r - 1 = \text{versh}\, r$; $4\pi k e^B = A$,

$$\frac{dN}{dr} = A \sinh^2 r \cosh r \, e^{B \,\text{versh}\, r}. \tag{7}$$

In the limiting case of small velocities, $r = \sinh r = \tanh r = v$, and the equation gives the simple Maxwell law already obtained where $A = \alpha$ and $B = -2\beta$. If we wish to get the general distribution law with respect to velocity, which, however, has no fundamental importance, we may write, since $d \tanh r = \text{sech}^2 r \, dr$,

$$\frac{dN}{dv} = A \sinh^2 r \cosh^3 r \, e^{B \,\text{versh}\, r}$$

$$= A \frac{v^2}{(1 - v^2)^{\frac{5}{2}}} e^{B\left(\frac{1}{\sqrt{1-v^2}} - 1\right)}. \tag{8}$$

Similarly it is obvious that we may obtain the distribution of N with respect to any of the other hyperbolic functions of r, and two of these have important physical significance, for $m_0 \sinh r = M$, the momentum of a particle; and $m_0 \cosh r = m$, its mass (or total energy); while $m_0 \,\text{versh}\, r = E$, the additional mass due to its motion (or its kinetic energy). Thus

$$\frac{dN}{d \sinh r} = A \sinh^2 r \, e^{B(\sqrt{1+\sinh^2 r} - 1)}, \tag{9}$$

$$\frac{dN}{dM} = \frac{A}{{m_0}^3} M^2 e^{B\left(\sqrt{1+\left(\frac{M}{m_0}\right)^2} - 1\right)}, \tag{10}$$

$$\frac{dN}{d \cosh r} = A\sqrt{\cosh^2 r - 1} \cosh r \, e^{B(\cosh r - 1)}, \tag{11}$$

$$\frac{dN}{dm} = \frac{A}{{m_0}^3}\sqrt{m^2 - {m_0}^2} \; m \; e^{B\left(\frac{m}{m_0} - 1\right)}, \tag{12}$$

$$\frac{dN}{d \,\text{versh}\, r} = A\sqrt{2 \,\text{versh}\, r + \text{versh}^2 r}(1 + \text{versh}\, r) \, e^{B \,\text{versh}\, r}, \tag{13}$$

$$\frac{dN}{dE} = \frac{A}{{m_0}^3}\sqrt{2m_0E + E^2} \, (m_0 + E) \, e^{\frac{BE}{m_0}} \tag{14}$$

Equation (10) shows the distribution of particles with respect to momentum, equation (12) with respect to mass or total energy, and equation (14) with respect to kinetic energy. These equations are in complete accord with the distribution equation obtained in a very different way by Jüttner.[1]

If we integrate any one of these equations over the entire range we may write the result equal to the total number of particles. Similarly an equation for the total kinetic energy can be obtained, and the constants A and B are thus determined in terms of those quantities. As shown by Jüttner, B can be very simply expressed by the equation

$$B = -\frac{m_0}{kT}, \tag{15}$$

while A has as yet been obtained only in terms of definite integrals which may be reduced to Bessel functions.

Tolman has already pointed out that in the case of a gas composed of particles of zero (infinitesimal) mass at rest the distribution equation assumes a simple, integrable form. Molecules of zero m_0 may have no physical significance, it is therefore important to note that the equations assume the same simple form for any molecules at very high temperatures. Thus equation (14), when m_0 is infinitesimal, or when T approaches infinity, assumes the form

$$\frac{dN}{dE} = \frac{A}{m_0^3} E^2 e^{-\frac{E}{KT}}.$$

This same equation results likewise from equations (10) and (12) for when $v = 1$, $E = M = m$. The constant A/m_0^3 is easily evaluated, since integration from zero to infinity gives $N = 2k^3T^3A/m_0^3$, whence

$$\frac{dN}{dE} = \frac{N}{2k^3T^3} E^2 e^{-\frac{E}{KT}}. \tag{16}$$

The total energy of particles whose individual energies lie between E and $E + dE$ is therefore

$$dU = EdN = \frac{N}{2k^3T^3} E^3 e^{-\frac{E}{KT}} dE. \tag{17}$$

The equations have been developed in this form for reasons which will be brought out in another place.

APPENDIX.

In order to prove that all the propositions of a certain geometry are applicable to a given spatial system, it suffices to show that the postulates of the geometry are valid for that space. The postulates of Lobat-

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[1] There is a slight confusion in Jüttner's paper owing to his designation of $m_0/\sqrt{1 - v^2}$, which is the total mass or energy, as "lebendige Kraft," but this does not affect seriously the important conclusions which he obtains.

schewskian geometry are known to be identical with those of Euclidean geometry except that the parallel postulate is replaced by the following:

Through any point not on a given straight line two and only two parallel (asymptotic) straight lines can be drawn.

From our knowledge of the non-Euclidean geometry of relativity we may readily show the validity of the Lobatschewskian postulates upon the surface of the pseudo-sphere, the intersections of which with planes drawn through the center of the pseudo-sphere are the "straight lines" of the space.

Since any two points on the surface of the pseudo-sphere, together with the center, determine one and only one plane, one and only one straight line can be drawn through any two points.

Since rotation about a line joining the center with any point on the surface leaves that point fixed and carries every other point through a closed path which is completely in the surface, and of which the radii in that surface are mutually congruent, the system obeys the Euclidean postulate of rotation.

It is evident from the construction of the surface that two straight lines are parallel (asymptotic) when and only when the two planes which determine them intersect in an element of the singular cone. The plane which determines a given line cuts the cone in two elements, each of which determines, together with any point outside the given line, a plane which intersects the surface in a line asymptotic to the given line. Thus in Fig. 3 the plane *A'O'D'* determines the line *AOD*. *P* represents

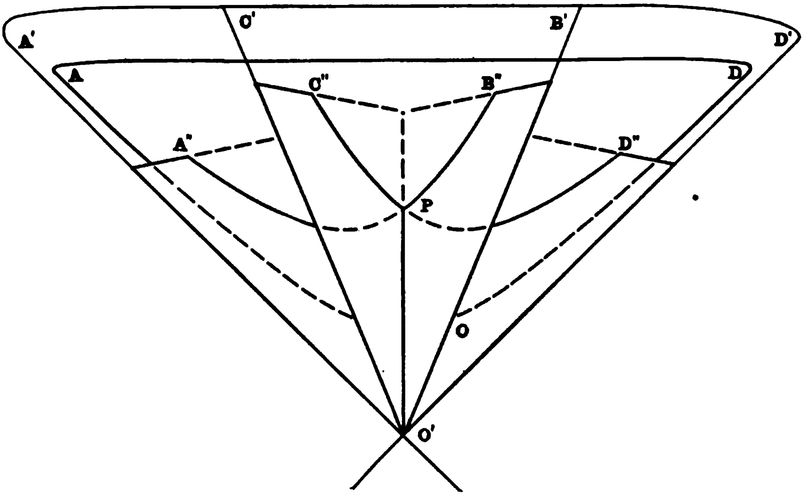

Fig. 3.

a point off this line and determines with $O'A'$ the plane $A'O'B'$ and hence the line $A''PB''$; likewise P determines with $O'D'$ the plane $C'O'D'$ and hence the line $C''PD''$. PA'' and OA are asymptotic to each other and to $O'A'$, and PD'' and OD are asymptotic to each other and to $O'D'$.

Such other minor postulates as are necessary to define completely the geometry, such as the infinite extension of the straight line, also follow obviously from the construction. Moreover, owing to the known identity of the Lobatschewskian with the log.-spherical geometry of Taurinus, it is evident that the constant of the space determined by a pseudo-sphere of unit radius is unity.

When we consider the hyper-pseudo-sphere with its three dimensional boundary we see that every intersection of this boundary with a planoid drawn through its center is a pseudo-sphere of unit radius. If we regard these intersections as Lobatschewskian "planes," then since any two intersecting lines determine a Lobatschewskian plane the space is Lobatschewskian.

This is not the place to dwell further upon the various interesting features of the geometrical constructions in this non-Euclidean geometry of relativity, but we believe that the one which we have just employed gives a far better picture of the properties of Lobatschewskian space than can be obtained by the aid of the figure constructed in Euclidean space which is also known as the pseudo-sphere. Thus, for example, one of the interesting figures in Lobatschewskian space, the horocycle (horosphere), is in our construction merely the intersection of the pseudo-sphere (hyper-pseudo-sphere) with a plane (planoid) parallel to a tangent plane (planoid) of the singular cone (hypercone). The surface of the other pseudo-sphere (of one sheet) which envelopes the singular cone also presents a most interesting geometry which has, we believe, not been discussed hitherto.

Chemical Laboratory of the University of California,
January 9, 1914.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

NEW YORK MEETING, FEBRUARY 27, 1915.

The seventy-sixth regular meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York, on Saturday, February 27, at 10:00 o'clock. The following papers were presented:

The Joule Free Expansion Experiment and the Correction of The Constant Volume Gas Thermometer. LYNDE P. WHEELER.

The Forms of Physical Equations. (By title.) E. BUCKINGHAM.

Electrical Characteristics of X-Ray Tubes. J. S. SHEARER and P. T. WEEKS.

Fluorescence and Absorption of Certain Organic Substances. R. C. GIBBS and K. GIBSON.

Absorption of Certain Glasses of Known Composition. K. GIBSON.

Fluorescence of Frozen Solutions of Uranyl Salts. (By title.) W. HOWES.

Fluorescence and Absorption of Uranyl Ammonium Chloride. EDWARD L. NICHOLS.

Response of a Silicon Detector to Short Electric Waves. ERNEST MERRITT.

Agglomeration Theory of Variation of Specific Heat of Solids with Temperature. A. H. COMPTON.

Construction of Crystals with Theoretical Atom. A. C. CREHORE.

Notes on the Atomic Nuclei. WILLIAM DUANE.

New Device for Rectifying High Tension Alternating Currents. SAUL DUSHMAN.

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